that observed in the previously analysed cinnamic acid derivatives in which nearest-neighbour >C=C< groups are parallel (related by translation) or antiparallel (related by centres of symmetry). The centre-to-centre distance of nearest-neighbour >C=C< groups is 3·93 Å; contacts between C(3) and C(4′) and C(3′) and C(4) of adjacent glide-plane related molecules are 3·53 Å and 4·33 Å respectively. It follows from these values that interaction between two molecules is possible and likely to take place in the first instance between C(3) and C(4′).

The *p*-derivative displays the packing arrangement of the α type in the cinnamic acid series since contacts between nearest-neighbour >C=C< groups occur across centres of symmetry. Three sets of such contacts are present (Fig. 4); the centre-to-centre distances across the inversion centres at $(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and $(0\frac{1}{2}0)$ are 4·11, 5·29, and 5·74 Å respectively. In the light of our previous results we should expect photochemical interaction across the centre at $(0\frac{1}{2}\frac{1}{2})$ with formation of the centrosymmetric dimer, dimethyl 4,4′-dibromo-α-truxillate.

We thank Prof. J. M. Robertson, F. R. S. and Dr S. A. Sutherland for permission to use their unpublished results on crotonic and sorbic acids. Our thanks are due to Mr. S. Filippakis for assistance with the experimental work. We gratefully acknowledge support of this work by the National Bureau of Standards, Washington, D.C., under contract NBS G-10.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.
Chatani, Y., Sakata, Y. & Nitta, I. (1963). *Polymer Letters*, **1**, 419.
Davies, D. R. & Pasternak, R. A. (1956). *Acta Cryst.* **9**, 334.
Ferguson, G. & Sim, G. A. (1961). *Acta Cryst.* **14**, 1262.
Ferguson, G. & Sim, G. A. (1962). *Acta Cryst.* **15**, 346.
Higgs, M. A. & Sass, R. L. (1963). *Acta Cryst.* **16**, 657.
International Tables for X-ray Crystallography (1962). Vol. III, p. 206. Birmingham: Kynoch Press.
Jong, A. W. K. de (1923). *Ber. dtsch. chem. Ges.* **56**, 818.
Liebermann, C. & Zsuffa, M. (1921). *Ber. dtsch chem. Ges.* **44**, 841.
McWeeny, R. (1951). *Acta Cryst.* **4**, 513.
Morrison, J. D. & Robertson, J. M. (1949*a*). *J. Chem. Soc.* p. 980.
Morrison, J. D. & Robertson, J. M. (1949*b*). *J. Chem. Soc.* p. 993.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
Phillips, D. C. (1956). *Acta Cryst.* **9**, 819.
Rabinovich, D. & Schmidt, G. M. J. (1964). *J. Chem. Soc.*, p. 2030.
Rossmann, M. G., Jacobson, R. A., Hirshfeld, F. L. & Lipscomb, W. N. (1959). *Acta Cryst.* **12**, 530.
Scheuerman, R. F. & Sass, R. L. (1962). *Acta Cryst.* **15**, 1244.
Schmidt, G. M. J. (1964). *J. Chem. Soc.*, p. 2014.
Schomaker, V., Waser, J., Marsh, R. E. & Bergman, G. (1959). *Acta Cryst.* **12**, 600.

Acta Cryst. (1965). **18**, 1067

The Crystal and Molecular Structure of D(+)-Barium Uridine-5′-Phosphate*

By Eli Shefter and K. N. Trueblood
Department of Chemistry†, *University of California*, *Los Angeles*, *California*, 90024, *U.S.A.*

(*Received* 24 *September* 1964)

The crystal structure of hydrated barium uridine-5′-phosphate has been determined by three-dimensional Patterson and Fourier syntheses. The anomalous scattering of Cu *K* radiation by the barium (and phosphorus) atoms made it possible to confirm the absolute configuration of the molecule. The structure was refined by block diagonal least squares which made use of two unique octants of intensity data by incorporating the complex parts of the atomic scattering factors. The final *R* value was 9·8 % for 1502 $hk\bar{l}$ and 1000 *hkl* intensity data.

The geometry and absolute configuration of the molecule are in accord with previous studies on nucleotides. The barium ions lie in two independent special positions and each ion is surrounded by ten oxygen atoms. The nucleotides pack compactly, with pairs of base planes nearly parallel but only partially overlapping, and a close contact of O(1′) of one molecule with the pyrimidine ring of another. The conformation about the C(5′)-C(4′) bond in ribose derivatives and related molecules has been considered in detail, and its bearing on nucleotide conformation discussed. A suggested hydrogen-bonding scheme is illustrated.

Introduction

Divalent metal ions, especially those of the alkaline earths, play a significant part in the combination and the structural relationships of proteins and nucleic acids. The role of such ions in liberating DNA from nucleoproteins has been demonstrated by Kirby (1957, 1958). Dipositive cations are also known to act as catalysts in biological reactions of triphosphate nucleosides.

Various possibilities of coordination of dipositive cations with nucleotides have been discussed by Brint-

---

* This work was supported in part by Public Health Service Research Grant A-3909 from the National Institute of Arthritis and Metabolic Diseases, Bethesda, Maryland.

† Contribution Number: 1723.

zinger (1961), but the only previously reported structure of a salt of a nucleotide with such an ion is that of calcium thymidylate (Trueblood, Horn & Luzzati, 1961). The present determination of the structure and absolute configuration of barium uridine-5′-phosphate provides further data on the biologically significant coordination of alkaline earth ions with nucleotides.

Experimental data and procedures

Barium uridine-5′-phosphate ($C_9H_{11}N_2O_9PBa$) was supplied to us by A. M. Michelson. It forms plate-like crystals, elongated along **b**, upon slow evaporation o aqueous solutions. When the crystals are taken from the solution they readily lose some water of hydration and start to show polycrystallinity within a few days. Crystals for data collection were therefore mounted in thin-walled boron-lithium glass capillaries.

Weissenberg and precession photographs with Cu $K\alpha$ radiation gave the following systematic extinctions, which indicate the space group to be $C222_1$: hkl, $h+k=2n+1$; $00l$, $l=2n+1$. The cell dimensions, determined from an $h0l$ Weissenberg photograph calibrated with CeO_2 ($a_0=5\cdot411$ Å) and from precession and oscillation photographs with the crystal mounted about **b**, were found to be:

$$a_0=21\cdot11\pm0\cdot02,\ b_0=9\cdot06\pm0\cdot03,\ c_0=20\cdot98\pm0\cdot02\ \text{Å}.$$

The density of the freshly crystallized material, determined by flotation in chloroform and bromoform, was found to be $2\cdot05\pm0\cdot01$ $g.cm^{-3}$. With the assumption that there are 8 formula weights of the salt in the unit cell, the volume and density then correspond to the presence of $8\cdot9\pm0\cdot2$ molecules of water per molecule of nucleotide. However, as noted below, only seven water molecules were actually found; presumably the crystal effloresced slowly during the recording of the data.

The difficulty in obtaining good crystalline specimens made it necessary to use one crystal for collection of all the intensity data. The dimensions of this crystal were 0·61 mm along **b**, 0·12 mm along **a**, and 0·36 mm along **c**. Intensity data ($h0l$ to $h6l$) were collected on equiinclination Weissenberg photographs with a Nonius integrating camera, nickel-filtered Cu $K\alpha$ radiation, and Ilford type-G industrial film. The photographs of the various layers were taken with the same exposure time in order to facilitate interlayer scaling.

Most of the intensities were measured with a Baird-Atomic microdensitometer (Model CB), but those too weak to be so determined were estimated visually with a calibrated integrated intensity strip. The integration process tended to blur together some of the weaker high-angle reflections, making it extremely difficult to determine their intensity, and consequently many reflections were considered undeterminable rather than unobservable and were not included in the analysis. In addition to the usual geometrical corrections, approximate absorption corrections were made with the program of C. Burnham (ACA No. 338) and absorption coefficients from *International Tables* (1962).

The anomalous scattering effect of the barium atoms made it advantageous to measure the intensities of reflections in two octants; the indexing method of Peerdeman & Bijvoet (1956) was used. The numbers of $hk\bar{l}$ and hkl reflections observed were 1502 and 1000 respectively, representing together approximately 53 percent of the data in the Cu$K\alpha$ sphere of reflection.

All calculations were made on an IBM 7090 computer. The form factors used for carbon, oxygen and nitrogen were those of Hoerni & Ibers (1954); that for phosphorus was Tomiie & Stam's (1958). The scattering curve for Ba^{2+} was approximated by using the curve for neutral Ba (Thomas & Umeda, 1957) above $\sin\theta/\lambda=0\cdot2$ and extrapolating this curve smoothly to 54 below this value. The anomalous dispersion corrections of Dauben & Templeton (1955) were applied to the atomic scattering factors of phosphorus and barium.

Determination of the structure

Although there is, on the average, only one barium ion per asymmetric unit, there are in fact two independent Ba^{2+} each lying on a twofold axis. They were located from a three-dimensional Patterson synthesis. One lies on the twofold axis at $(0, y, \frac{1}{4})$ and the other on that at $(x, 0, 0)$. The positions of the other atoms of the nucleotide were found in a three-dimensional Fourier synthesis phased on the two barium ions, which represent 62% of the scattering matter on a Z^2-basis. Successive Fourier syntheses phased on the barium ions and other atoms of the molecule showed seven water molecules per asymmetric unit, six of them lying in general positions and the other in two sets of special positions on the twofold axis parallel to **b** at $(0, y, \frac{1}{4})$. All of the $(hk\bar{l})$ data, but not the (hkl) data, were used in all Fourier summations.

Refinement

The observed anomalous scattering effect was sufficiently large that changes were made in the usual least-squares equations to permit using the independent $(hk\bar{l})$ and (hkl) data. The least-squares equations were derived in the usual way from the appropriate expressions for $F(hk\bar{l})$ and $F(hkl)$ (*e.g.* Patterson, 1963).

After the positions of all the atoms with the exception of the water molecules at $(0,y,\frac{1}{4})$ had been well defined by Fourier syntheses, three cycles of block-diagonal least-squares refinement were calculated with individual isotropic temperature factors in order to improve the interlayer scaling which was initially based only on relative exposure time. In these and all suceeding cycles the function minimized was $\Sigma w(F_o-G|F_c|)^2$, where G is the scale factor for the calculated structure factors. The least-squares program was that of Gantzel, Sparks & Trueblood (ACA No. 317). Hughes's weighting scheme (1941) was used throughout the refinement. The final layer scaling after this initial refinement required a maximum adjustment of about 20%, with the average change in relative scale only about 5%.

After the seventh water molecule was ascertained to be divided between the special positions along the twofold axis at $(0, y, \frac{1}{4})$, block-diagonal least-squares refinement was carried out with all the data, with the barium and phosphorus atoms assigned anisotropic temperature factors. The shifts in the final cycle were less than one-third of the standard deviations estimated from the diagonal elements of the matrix of the least-squares normal equations. The final value of the usual discrepancy index, R, was 9·8% for 2502 observed reflections. Table 1 gives the final fractional coordinates and e.s.d.'s obtained from the final cycle of least squares. Table 6 contains a list of the observed (F_o) and calculated (F_c) structure factors for the $(hk\bar{l})$ and (hkl) data.

Absolute configuration

The absolute configuration of the compound was easily determined by comparison of the calculated structure factors for both enantiomorphs. The results are in accord with previous conclusions concerning the absolute configuration of D(+)-ribose. Table 2 lists some of the reflections showing large differences between the observed structure factor and that calculated for the L-form. Near the end of the refinement, the overall reliability factor for the D(+) form was significantly lower than that for the L(−) form (10·8% and 14·3% respectively).

Table 1. *Positional and thermal parameters and their estimated standard deviations**

	x	y	z	B
Ba(1)	0	501(2)	2500	†
Ba(2)	489(1)	0	0	†
P	1264(2)	5719(7)	1609(2)	†
O(I)	1316(8)	7414(22)	1506(9)	4·3(0·3) Å^2
O(II)	941(8)	5456(25)	2238(9)	4·7(0·3)
O(III)	955(8)	4807(26)	1089(9)	5·0(0.4)
O(2′)	2006(6)	5197(19)	1678(6)	2·9(0·2)
C(5′)	2177(9)	3675(26)	1767(9)	2·7(0•3)
C(4′)	2873(11)	3673(33)	1759(12)	4·0(0·5)
C(3′)	3219(8)	4723(29)	2247(9)	2·8(0·3)
C(2′)	3384(8)	6012(28)	1804(9)	2·7(0·3)
C(1′)	3511(8)	5314(26)	1139(8)	2·4(0·3)
O(1′)	3102(6)	4057(19)	1124(7)	2·8(0·2)
O(3′)	3777(7)	4052(19)	2458(8)	3·7(0·3)
O(2′)	3890(7)	6813(21)	2037(7)	3·5(0·3)
N(3)	3658(7)	8005(21)	−135(7)	2·4(0·3)
C(2)	3858(8)	6901(27)	293(10)	2·7(0·3)
O(2)	4408(6)	6538(19)	367(7)	3·4(0·3)
N(1)	3351(7)	6302(21)	630(8)	2·4(0·3)
C(6)	2723(9)	6610(26)	497(9)	2·6(0·3)
C(5)	2560(7)	7588(28)	75(9)	2·2(0·3)
O(4)	2916(6)	9257(18)	−738(6)	2·8(0·2)
C(4)	3026(8)	8286(27)	−300(10)	2·7(0·3)
Water (1)	970(8)	7109(22)	−49(9)	4·3(0·3)
Water (2)	627(9)	1668(26)	1403(10)	5·2(0·4)
Water (3)	155(8)	8649(24)	1148(9)	5·0(0·4)
Water (4)	1590(7)	−140(23)	874(7)	3·9(0·3)
Water (5)	319(10)	5646(30)	4145(11)	6·2(0·5)
Water (6)	1297(7)	4467(22)	3334(8)	4·1(0·3)
Water (7)	0	3479(54)	2500	10(1)
Water (8)	0	7361(55)	2500	10(1)

* x, y, z times 10^4. The numbers in parentheses following each value are the e.s.d.'s.

† These three atoms were refined anisotropically; the final values of the coefficients, × 10^4, with their e.s.d.'s were:

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ba(1)	11(0·3)	79(3)	30(1)	0	−5(1)	0
Ba(2)	11(0·3)	99(4)	21(0·4)	0	0	25(2)
P	13(1)	81(10)	14(1)	−1(4)	1(1)	1(4)

Results and discussion

The structural parameters found in this work have higher e.s.d.'s than those in most other reported investigations of nucleotides because of the presence of the barium ions. These ions not only dominate the scattering, but also cause large absorption errors, which are undoubtedly not entirely corrected. The e.s.d.'s average about 0·03 Å for the bonds between the light atoms, and about 2° for the angles involving these atoms. All the intramolecular bond distances and angles are shown in Fig. 1; the numbering system used is that of *Chemical Abstracts*.

The geometry found for the phosphate group in this molecule agrees, within the 95% confidence level of twice the e.s.d., with that found in calcium thymidylate (Trueblood, Horn & Luzzati, 1961), cytidylic acid (Alver & Furberg, 1959), adenosine-5′-phosphate (Kraut & Jensen, 1963) and 2-aminoethanol phosphate (Kraut, 1961). The conformation of the phosphate group in relation to the sugar is also of interest; Furberg (1960) has discussed the conformational possibilities, with emphasis on the consequent differences in extension of the molecule. It is noteworthy that in the known ribose and deoxyribose phosphates with the 5′ linkage (calcium thymidylate, barium ribose-5-phosphate, adenosine-5′-phosphate, and the present molecule), the phosphate group is fully extended with the P–O ester bond nearly parallel to the C(4′)–C(5′) bond.

A parameter that appears even more significant concerns the conformation about the C(5′)–C(4′) bond (of a furanose). After the essence of the following discus-

Table 2. *Comparison of F_o with $|F_c|$ for* D- *and* L-*forms of barium uridine phosphate**

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$L	$\lvert F_c\rvert$D
$13\bar{1}$	156	112	141
421	122	153	112
$42\bar{1}$	159	112	153
911	96	133	115
$73\bar{1}$	171	213	194
441	237	168	195
151	47	89	49
$15\bar{1}$	86	49	89
351	213	175	197
$35\bar{1}$	154	197	175
551	171	126	150
912	272	332	289
1422	111	171	129
932	141	191	153
$51\bar{3}$	180	135	179
753	180	124	142

* Near the end of the refinement

sion had been written we received an unpublished manuscript (Sundaralingam, 1964) concerned with the conformations of furanoside rings in which he had also considered the orientation of the C(5′)–O(5′) bond, and had made calculations for six of the compounds in Table 3, including two for which data were unavailable to us. Fig. 2 is a schematic view along the C(5′)–C(4′) bond showing the approximate conformation in the present molecule and other ribose derivatives. For convenience in comparing different structures we define two dihedral angles, as in Fig. 2: φ_{OO} between the projected C(5′)–O(5′) and C(4′)–O(1′) bonds, and φ_{OC} between the projected C(5′)–O(5′) and C(4′)–C(3′) bonds. When the conformation about the C(5′)–C(4′) bond is similar to that in Fig. 2 then both of these angles will be in the neighborhood of 60°, *i.e.* C(5′)–O(5′) is *gauche* to both C(4′)–O(1′) and C(4′)–C(3′); in either of the other two possible staggered conformations, one of the two angles would be near 180°. Table 3 gives the values of these angles in a variety of ribose and deoxyribose derivatives, as well as in some hexoses with pyranose as well as furanose rings. The compounds vary widely; yet it is remarkable how similar the values of these angles turn out to be. Quite clearly the conformation of Fig. 2 is the preferred one for exocyclic $-CH_2O-$ groups in furanose derivatives, regardless of whether or not the oxygen atom is esterified or is involved in hydrogen bonding; it is the only conformation that has been reported for nucleotides, whether *β*- or *α*-. The reason why this conformation seems preferred is not clear. It may be relevant that ethylene glycol and ethylene chlorohydrin (in the vapor phase) have the *gauche* rather than the *trans* conformation, with the dihedral angle about 74° (Bastiansen, 1949), while 1,2-dichloroethane (Ainsworth & Karle, 1952) is predominantly *trans*. Bastiansen has attributed this to intramolecular hydrogen bonding, even though the O–H · · · O angle would be in the neighborhood of 110–120°; in any event, that explanation cannot suffice for all the present compounds since many of them are esterified at O(5′) (unless it is argued that the free sugars are in this conformation because of intramolecular hydrogen bonding and that after the esters are formed the barrier to rotation about these bonds is abnormally high so that other conformers do not form). Furthermore, this explanation would not suffice to eliminate *gt* conformers (Table 3).

Whatever the explanation of the preference for the *gg* conformation about C(5′)–C(4′) (Table 3), it has important implications for *β*-ribo- and *β*-deoxyribonucleotides. In the *β*-configuration, the glycosidic bond and the C(4′)–C(5′) bond are on the same side of the furanose ring, as is evident in Fig. 1. Because of the position taken by the O(5′) atom, there is limited room for the bulkier parts of the purine or pyrimidine ring in different conformations about the glycosidic C(1′)–N bond. Any bulky substituent on the atom adjacent to the glycosidic N atom interferes with O(5′), as is evident from models. It is apparently in part for this reason that only *anti* conformations about the glycosidic C–N bond (Donohue & Trueblood, 1960) are found for *β*-nucleotides. The torsion angle about this bond is −43° in the present molecule.

Another factor which may help to stabilize *anti* conformations of *β*-nucleotides is the possible contribution of C–H · · · O hydrogen bonding (Sutor, 1963), especially in the *anti* conformations of pyrimidine nucleotides, such as the present one. The possible interaction is between the hydrogen on C(6) of the pyrimidine ring and O(5′) of the sugar. The C(6) · · · O(5′) distance is 3·17 Å in the present molecule, and although the hydrogen atom on C(6) has not been located, it must lie close to the C · · · O line; in the uridine residue of adenosine–uridine phosphate (Shefter, Barlow, Sparks & Trueblood, 1964), the corresponding

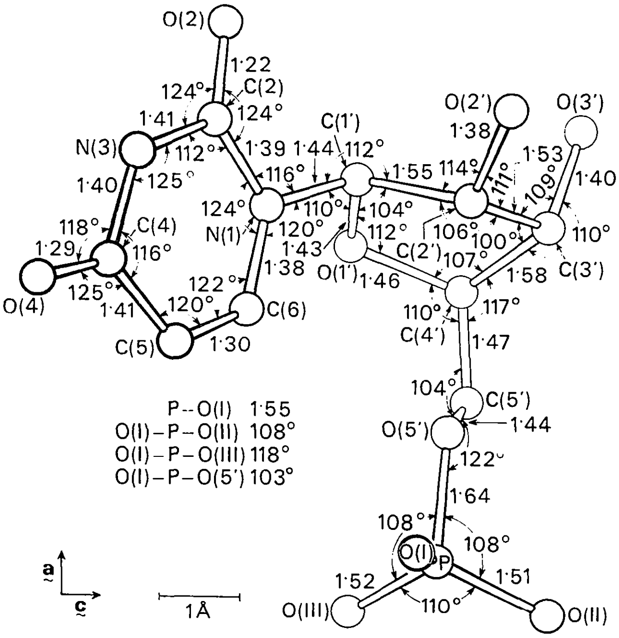

Fig. 1. Bond distances and angles in the nucleotide. The actual conformation of the molecule in the crystal is shown as viewed down **b**.

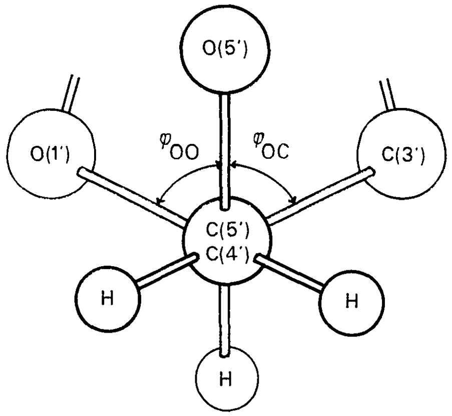

Fig. 2. Schematic projection down the C(5′)–C(4′) bond, showing the dihedral angles φ_{OO} and φ_{OC}.

C · · · O distance is 3·18 Å, with the H · · · O distance 2·3 Å, and the C–H · · · O angle 142°. In the calcium salt of thymidine-5′-phosphate (Trueblood, Horn & Luzzati, 1961), the corresponding distances and angle are 3·42 Å, 2·4 Å and 169°. All of these values agree quite plausibly with those suggested by Sutor (1963) as characteristic of C–H · · · O hydrogen bonding in analogous systems.

Sundaralingam (1964) has suggested that differences in furanose ring conformation may play a role in the variations of the glycosidic torsion angles in nucleosides and nucleotides.

Least-squares planes passing through the furanose ring of the present molecule were calculated for all five possible sets of four atoms; the combination giving the most satisfactory solution was the one with C(1′), C(3′), C(4′), and O(1′) coplanar and C(2′) out of the plane by 0·52 Å (Table 4). This result is in accord with the conformation in barium ribose-5-phosphate (Furberg & Mostad, 1960), and with the general conclusions of Spencer (1959) concerning the puckering of the ribose. None of the bond angles and distances in the ribose molecule differ from the values reported in other nucleotide and nucleoside structures by more than twice their e.s.d.'s.

The uracil ring has essentially the same bond angles and lengths as those found in calcium thymidylate, 5-fluoro-2′-deoxy-*β*-uridine (FUDR), (Harris & Macintyre, 1964), uracil (Parry, 1954), thymine (Gerdil, 1961), the complex of *N*-methyluracil with *N*-ethyladenine (Mathews & Rich, 1964), and *β*-adenosine-2′-*β*-uridine-5′ phosphoric acid (Shefter *et al.*, 1964). The C(4)–O(4) bond appears long, 1·29 Å, compared to the same bond in the above structures, average value 1·23 Å. However, this bond length has an e.s.d. of 0·03 Å, the position of C(4) being especially uncertain, so the difference is not significant. It is noteworthy that the C–C–O angle at C(4) is appreciably larger than the N–C–O angle here, just as it is in uracil itself, in *N*-methyluracil, and in the uracil residue of the above-cited adenosine-uridine phosphate, although in fluorodeoxyuridine the angles are equal. This same difference in the corresponding angles in thymine and its derivatives has been attributed to repulsion of the methyl group on C(5) and the oxygen atom, but this explanation now seems specious.

The six atoms comprising the uracil ring are coplanar (plane II of Table 4), with none of the ring atoms displaced from the least-squares plane by more than twice its e.s.d. Atom C(1′) of the ribose ring is 0·12 Å above the plane and O(2) is 0·14 Å below this plane, while O(4) is coplanar with the ring. The opposing displacement of O(2) and C(1′) was also found in calcium thymidylate. This effect may be partly, if not wholly, due to steric hindrance between the sugar and the base. The dihedral angle between the plane of the furanose ring and the uracil ring is 67°, a value very similar to that in all other known nucleotide structures.

The packing of the bases and sugars is illustrated in part in Fig. 5. Because the base planes lie nearly

Table 3. *Conformation about* C(5′)–C(4′) *bond**

Compound	φ_{OO}	φ_{OC}	Conformation†	Comment	Reference
Barium uridine-5′-phosphate	54°	70°	*gg*		This work
Cytidine-3′-phosphate	75	44	*gg*		Sundaralingam & Jensen (1964)
Adenosine-5′-phosphate	78	40	*gg*		Kraut & Jensen (1963)
Deoxyadenosine	68	173	*gt*	Deoxyribose	Watson, Sutor & Tollin (1963)
Calcium thymidine-5′-phosphate	63	57	*gg*	Deoxyriboside	Trueblood, Horn & Luzzati (1961)
Barium ribose-5-phosphate	67	56	*gg*		Furberg & Mostad (1962)
β-Adenosine-2′ *β*-uridine-5′-phosphate	73	45	*gg*	Adenosine residue	Shefter *et al.* (1964)
	62	57	*gg*	Uridine residue	
5-Fluoro-2′-deoxyuridine	173	68	*tg*	Deoxyribose	Harris & Macintyre (1964)
Vitamin B_{12} (air-dried)	60	66	*gg*	α-Riboside and 3′-phosphate linkage	Hodgkin *et al.* (1962)
α-D-glucose	66	172	*gt*	Glucopyranose	McDonald & Beevers (1952)
β-D-glucose	61	58	*gg*	Glucopyranose	Ferrier (1963)
Sucrose‡	58	60	*gg*	Glucopyranose	Beevers & Cochran (1947)
	74	38	*gg*	Fructofuranose, C(6′)–C(5′)	
	51	64	*gg*	Fructofuranose, C(1′)–C(2′)	
Cellobiose	33	168	*gt*	Glucopyranose	Jacobson, Wunderlich & Lipscomb (1961)
	62	180	*gt*	Glucopyranose	

* C(6′)–C(5′) in the hexoses, except as noted for fructose residue of sucrose. With the exception of the values for cytidine-3′-phosphate and deoxyadenosine, reported to us by Sundaralingam (1964), all values given were calculated by us from parameters in the references cited.

† The letters *g* and *t* refer to the terms *gauche* and *trans*, to signify whether the values of the dihedral angles of Fig. 2 are near 60° or near 180°; the first refers to φ_{OO} and the second to φ_{OC}.

‡ In sucrose sodium bromide dihydrate, but the conformations are the same about C(6)–C(5) of both residues in crystalline sucrose (Brown & Levy, 1963), although differing by 135° around C(1′)–C(2′) of the fructose residue. It is noteworthy that C(2′) in fructose has no hydrogen atoms, the lower hydrogen atom in the view analogous to Fig. 2 being replaced by a second (ether) oxygen atom, linked to the glucose residue.

parallel to **a** (Table 4), the pairs of bases related by the twofold axis along **a** at (x, $\frac{1}{2}$, 0) are nearly parallel to one another, as illustrated in the lower part of Fig. 5. The angle between them is just 4°; O(4) of one ring is only 3·12 Å from O(4), and 3·27 Å from C(5), of the other. All other contacts are greater than 3·3 Å.

An even closer intermolecular contact is between O(1′) of one molecule and the pyrimidine ring of a second related by the twofold axis along **a** at (x, 0, 0) which passes through Ba(2). This is also illustrated in Fig. 5; the base planes themselves are not close, but O(1′) is seen to project toward the other base, being only 2·74 Å from C(4), 3·02 Å from N(3), and 3·14 Å from both C(5) and O(4). This arrangement is found also for both sugars and both bases in adenosine-uridine phosphate (Shefter *et el.*, 1964), although none of the contacts there is as short as the O(1′) · · · C(4) distance here. Close contacts of this sort between carbonyl oxygen atoms and carbonyl carbon atoms in nearby molecules have been noted frequently (*e.g.* Bolton, 1963), although few as short as the present one have been reported.

Barium coordination

The barium ions lie in two independent special positions in the structure. The ions in each of these positions have eight nearest-neighbor oxygen atoms at distances between 2·7 and 3·0 Å and two next-nearest neighbors at 3·3 Å; thus the total coordination number around the two unique barium ion positions is ten. The environments of the ions are illustrated in Figs. 3 and 5, and the Ba–O contact distances are listed in Table 5. The eight nearest oxygen neighbors of the barium ions are arranged in a distorted square Archimedean antiprism, with the two longer bonds extending out from triangular faces.

Ba(1), located on the twofold axis at (0, y, $\frac{1}{4}$), is coordinated directly to two hydroxyl groups in each of

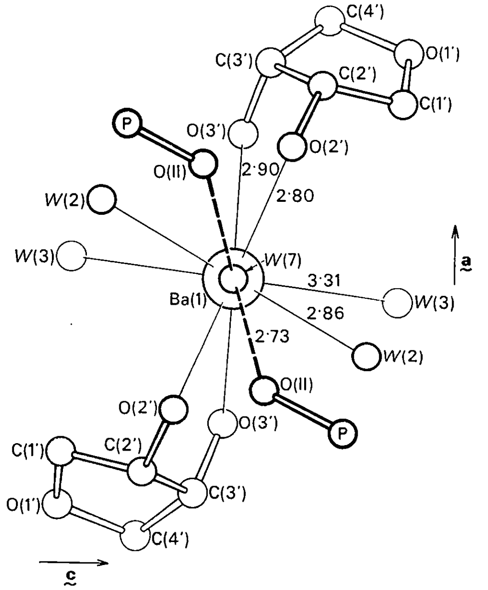

Fig. 3. The environment of Ba(1), viewed down **b**.

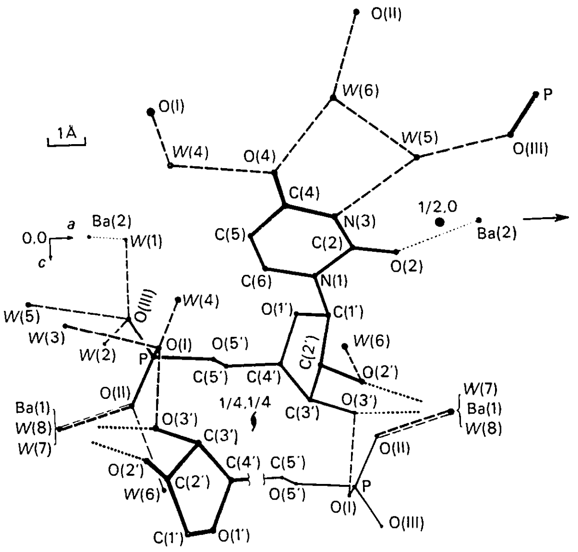

Fig. 4. Suggested hydrogen-bonding scheme and view of the molecule along **b**

Table 4. *Least-squares* planes of ribose and uracil residues*

Coefficients†	Atoms comprising the plane	Displacements	Displacements of other atoms	
$A=$ 0·7737	C(1′)	−0·02 Å	C(2′)	−0·52 Å
$B=-$0·6292	O(1′)	0·03	O(2′)	−0·11
$C=$ 0·0745	C(3′)	0·02	O(3′)	1·34
$D=-$2·900	C(4′)	−0·03	C(5′)	−1·16
			N(1)	−0·92
$A=$ 0·0288	N(1)	0·02	O(2)	−0·14
$B=$ 0·7250	C(2)	−0·04	O(4)	−0·04
$C=$ 0·6882	N(3)	0·05	C(1′)	0·12
$D=-$5·232	C(4)	−0·04		
	C(5)	0·02		
	C(6)	−0·01		

* All planes were calculated in a manner similar to that described by Schomaker, Waser, Marsh & Bergman (1959).

† These are coefficients for the equation of the plane in the form $AX+BY+CZ+D=0$, with X, Y, and Z in Å measured along **a**, **b**, and **c***.

two ribose molecules. The Ba(1) to O(3′) and O(2′) distances are 2·90 and 2·80 Å, respectively. Brintzinger (1961) in his discussion of divalent metal complexes of nucleotides suggested the possibility of this type of coordination. A similar coordination of Ba^{2+} has also been observed in barium ribose-5-phosphate (Furberg & Mostad, 1962), although there the Ba^{2+} is coordinated also to the hydroxyl group on C(1′), not present here. Ba(1) is also bonded to four water molecules at distances of 2·7 to 2·9 Å and another two water molecules at 3·31 Å.

Ba(2), located on the twofold axis at (x, 0, 0), is coordinated with two O(2) atoms on different uracil rings. This separation is 2·78 Å. There are six water molecules at distances of 2·8 to 3·0 Å from this barium ion, and two more at 3·32 Å. The Ba–O distances and arrangements found here are consistent with those reported previously (Nardelli & Fava, 1962; Furberg & Mostad, 1962); the coordination number of barium with oxygen typically ranges from nine to twelve, with the average distance increasing as the coordination number increases.

The coordination polyhedra of the barium ions are linked together by the mutual bonding of the barium ions to waters (2) and (3). Water (2) is at 2·86 Å from Ba(1) and 3·32 Å from Ba(2), while water (3) is 2·79 Å from Ba(2) and 3·31 Å from Ba(1).

The barium ions are not linked directly to the phosphate oxygen atoms, but are connected to them through water bridges. These are of the type

$$\mathrm{Ba}\cdots\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{O}}\text{–}\mathrm{H}\cdots\mathrm{O}\text{–}\mathrm{P}\text{–}\,,$$

which are similar to those found in the barium ribose-5-phosphate structure. This type of bonding, rather than the direct bonding of the metal ion to the phosphate oxygen atoms as found in calcium thymidylate, was suggested by Brintzinger, on the basis of equilibrium studies of the bonding of Co^{2+}, Ni^{2+}, and Zn^{2+} in adenosine triphosphate systems. However, it should be noted (Furberg & Mostad, 1962) that deoxyribonucleotides, such as thymidine-5′-phosphate, have only one free sugar-hydroxyl group to coordinate with any cation present, while ribonucleotides have two (and ribonucleosides three).

Hydrogen bonding

Some features of the network of hydrogen bonds remain uncertain because no effort was made to locate the hydrogen atoms. The most probable hydrogen bonds are listed in Table 5, with pertinent distances and angles, and many of them are illustrated in Figs. 4 and 5, where they are designated by dashed lines. We have avoided so designating any short interaction which forms the edge of a barium coordination polyhedron for, as Templeton (1960) and Clark (1963) have pointed out, it is unlikely that protons will lie along these edges, especially if other positions are available to them. Only two interactions of this sort are smaller

Table 5. *Barium–oxygen contacts and possible hydrogen bonds*

Atom *A*	Atom *B*	Distance*	Some relevant angles	
Ba(1)	O(2′)	2·80 Å (2)		
	O(3′)	2·90 (2)		
	W(2)	2·86 (2)		
	W(3)	3·31 (2)		
	W(7)	2·70 (1)		
	W(8)	2·85 (1)		
Ba(2)	O(2)	2·78 (2)		
	W(1)	2·81 (2)		
	W(2)	3·32 (2)		
	W(3)	2·79 (2)		
	W(4)	2·96 (2)		
O(I)	O(3′)	2·64	C(3′)–O(3′) ··· O(I)	115°
	W(3)	2·80		
	W(4)	2·65		
O(II)	*W*(6)	2·58		
	W(7)	2·73	O(II) ··· *W*(7) ··· O(II)′	98
	W(8)	2·69	O(II) ··· *W*(8) ··· O(II)′	100
O(III)	*W*(1)	2·79		
	W(2)	3·00		
	W(5)	2·84		
O(2′)	*W*(6)	2·56	C(2′)–O(2′) ··· *W*(6)	105
N(3)	*W*(5)	2·91	C(2)–N(3) ··· *W*(5)	120
			C(4)–N(3) ··· *W*(5)	114
W(3)	*W*(5)	2·96	O(I) ··· *W*(3) ··· *W*(5)	89
W(4)	O(4)	2·93	O(I) ··· *W*(4) ··· O(4)	119
W(6)	*W*(5)	2·88	O(III) ··· *W*(5) ··· *W*(6)	118
	O(4)	2·81	*W*(6) ··· *W*(5) ··· *W*(3)	118
			O(II) ··· *W*(6) ··· *W*(5)	101
			O(II) ··· *W*(6) ··· O(4)	131
			W(5) ··· *W*(6) ··· O(4)	81

* The number in parentheses after each Ba–O distance gives the number of equivalent contacts of this sort.

than 3·0 Å: $W(2) \cdots W(4)$, 2·84 Å, and $O(2') \cdots W(7)$, 2·95 Å.

Each of the three phosphate oxygen atoms, O(I), O(II), O(III), appears to accept three hydrogen bonds. Each set of hydrogen-bonded neighbors is so arranged as to form with the phosphorus a distorted tetrahedron. The average lengths of the bonds to O(I) and O(II) are 2·7 Å whereas the three hydrogen-bonds to O(III) average 2·9 Å. The eight unique water molecules found in this structure are each involved in a hydrogen bond to a phosphate oxygen atom; the ninth bond comes from O(3′) of the ribose. O(2′) also appears to donate its hydrogen atom in a short hydrogen bond to water molecule *W*(6).

The hydrogen atom on N(3) of the uracil ring is directed towards *W*(5), 2·91 Å away. Water molecules (4) and (6) are 2·93 and 2·86 Å from O(4) of the uracil ring. From the angles around the water molecules it appears likely that there is a hydrogen bond between *W*(4) and O(4). *W*(5) and *W*(6) are the only two water molecules not coordinated to a barium ion, but each of them has four neighbors at reasonable distances for hydrogen bonds. The two water molecules in special positions, *W*(7) and *W*(8), have very high temperature factors, and may well be somewhat disordered, especially in view of their high apparent coordination numbers if they occupy the exact twofold position. Structure factor calculations with models containing disordered water molecules somewhat off the twofold axes were inconclusive.

As mentioned earlier, the fresh crystal appears to contain two more water molecules per asymmetric unit than were actually found in our Fourier syntheses. Furberg & Mostad (1962) reported that some water molecules appeared to be lost from crystals of barium ribose-5-phosphate during photography. We have not succeeded in unequivocally identifying regions in the present structure from which water molecules might have migrated, although there may be room for one along the crew axis at ($\frac{1}{4}$, y, $\frac{1}{4}$). The molecule spirals about this axis, and water molecules might be trapped here initially but not held firmly. We attempted to measure the density of our single specimen after the collection of the intensity data, but because of apparent decomposition succeeded only in establishing that it was in the neighborhood of 1·9 g.cm^{-3}. Since the crystals with nine water molecules per molecule of salt contain 26% water, the loss of two water molecules would reduce

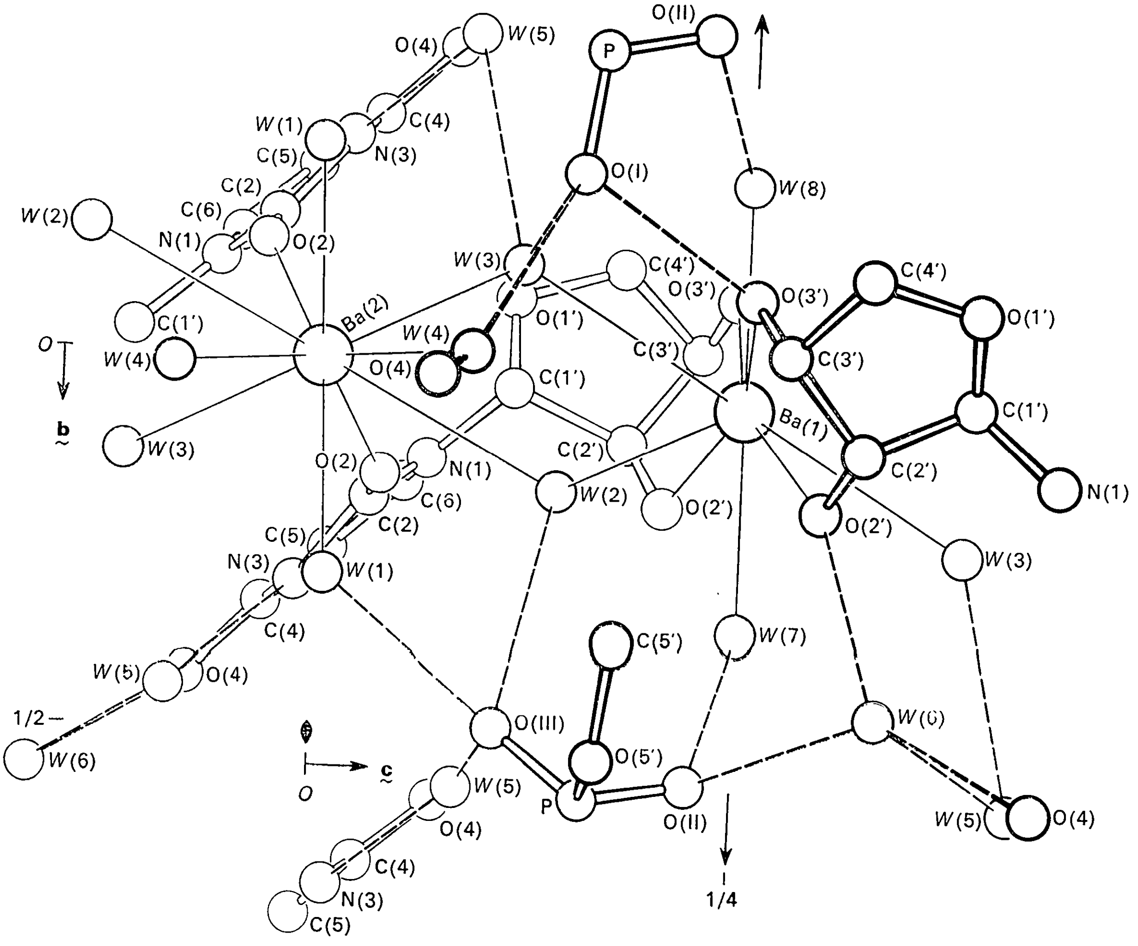

Fig. 5. A portion of the structure viewed down **a**, showing the coordination around the barium ions and some possible hydrogen bonds (dashed lines).

Table 6. Observed and calculated structure factor amplitudes.
The three columns are, respectively, l, F_o, and $|F_c|$

H= 0, K= 0		
-4	265	312
-6	105	113
-8	326	354
-12	286	355
-16	106	105
-18	97	88
-20	69	71
-24	51	73
H= 2, K= 0		
0	350	243
-1	41	27
-2	94	100
-3	71	92
-4	311	358
-6	157	148
-7	257	268
-8	358	428
-9	84	68
-12	116	133
-13	188	189
-16	58	108
-19	88	86
-24	28	45
H= 4, K= 0		
0	28	88
-1	327	370
-2	46	26
-3	140	135
-4	235	246
-5	151	132
-6	252	256
-7	169	160
-8	151	152
-9	225	251
-10	54	48
-11	63	62
-12	94	80
-13	99	98
-14	58	65
-15	121	116
-16	145	150
-17	130	131
-18	47	50
-19	47	59
-20	33	36
H= 6, K= 0		
0	188	201
-1	42	37
-2	255	291
-3	127	119
-4	32	30
-5	260	265
-6	317	322
-7	158	183
-8	51	63
-9	181	172
-10	161	156
-11	118	123
-12	105	105
-13	43	37
-14	143	135
-15	118	108
-16	47	43
-17	79	91
-18	60	55
-21	46	45
-22	44	54
-23	41	34
H= 8, K= 0		
0	159	175
-1	42	64
-2	385	385
-3	150	137
-4	118	95
-5	39	43
-6	158	156
-7	56	56
-8	116	93
-9	41	39
-10	225	223
-11	45	36
-12	111	104
-13	45	45
-14	128	129
-15	50	61
-18	50	65
-22	77	89
H= 10, K= 0		
0	132	102
-2	352	379
-3	109	98
-4	70	43
-6	286	282
-7	57	60
-9	47	46
-10	184	169
-14	147	169
-15	53	42
-18	67	81
-22	64	73
H= 12, K= 0		
0	105	113
-1	19	29
-2	202	200
-4	74	71
-5	25	34
-6	342	338
-8	61	65
-9	40	38
-10	103	85
-11	57	41
-12	76	68
-13	55	47
-14	93	92
-15	31	41
-16	35	49
-17	29	24
-18	73	76
H= 14, K= 0		
0	83	52
-1	73	69
-2	149	169
-3	109	112
-6	99	103
-7	133	141
-8	27	24
-9	30	47
-10	189	169
-11	56	75
-12	68	63
-13	120	107
-14	110	102
-15	71	63
-16	29	24
-17	62	53
-18	60	52
-19	75	77
H= 16, K= 0		
0	164	174
-1	72	83
-2	107	113
-3	135	138
-4	117	121
-5	57	58
-7	91	101
-8	145	148
-9	84	96
-10	119	124
-11	58	59
-12	66	67
-13	66	58
-14	31	44
-15	60	65
-20	35	44
H= 18, K= 0		
0	167	163
-1	53	61
-2	37	34
-3	123	120
-4	175	171
-5	85	86
-6	56	43
-7	21	37
-8	83	79
-9	109	100
-10	40	31
-11	40	49
-12	71	75
-13	38	22
-15	33	39
-16	70	77
H= 20, K= 0		
0	144	138
-4	155	163
-5	19	29
-6	19	20
-8	130	146
-10	60	55
-12	77	74
-16	51	86
H= 22, K= 0		
0	102	111
-3	46	45
-4	121	124
-8	126	124
-9	41	42
-12	65	76
-13	31	32
H= 24, K= 0		
0	136	112
-1	89	72
-2	70	47
-3	50	43
-4	88	72
-5	71	56
-7	56	48
-8	52	46
-9	68	52
-10	48	41
-11	37	34
-12	58	101
H= 26, K= 0		
0	37	25
-1	71	56
-2	64	53
-4	42	34
-5	50	44
-6	74	64
-7	49	47
H= 1, K= 1		
1	97	85
-1	77	61
2	100	72
-2	100	72
3	290	305
-3	264	290
-4	344	381
-5	102	106
6	99	87
-6	53	90
7	95	77
-7	75	58
8	308	330
-8	290	315
9	63	61
-9	64	60
10	41	29
-10	49	33
11	80	76
-11	65	61
12	112	102
-12	136	137
13	65	57
-13	77	71
-15	97	97
-16	179	181
-17	61	47
-18	63	46
-19	65	43
-20	80	84
-21	45	39
-22	14	25
-24	54	38
H= 3, K= 1		
0	261	251
1	154	147
-1	124	130
2	128	124
-2	141	146
3	119	111
-3	131	129
4	237	225
-4	253	259
5	115	113
-5	124	123
6	215	204
-6	223	208
7	185	176
-7	172	169
8	204	199
-8	197	190
9	178	167
-9	131	125
10	126	117
-10	120	115
11	152	150
-11	146	151
12	215	201
-12	202	195
13	53	55
-13	88	83
15	58	52
-15	88	74
16	61	60
-16	82	80
-17	76	77
-20	65	61
-21	64	53
-22	44	43
-23	56	50
-24	65	70
H= 5, K= 1		
0	417	295
1	229	230
-1	247	251
2	259	259
-2	207	225
3	142	135
-3	177	181
4	168	166
-4	111	116
5	132	124
-5	122	127
6	129	121
-6	145	144
7	164	163
-7	167	161
8	204	198
-8	198	202
9	174	159
-9	170	157
10	50	85
-10	127	130
11	150	146
-11	180	178
12	56	47
-12	62	66
13	130	124
-13	128	128
14	85	79
-14	81	77
15	55	85
-15	54	85
-16	31	36
17	50	88
-17	102	92
-18	33	38
-19	67	69
-20	46	41
-21	32	27
-25	44	37
H= 7, K= 1		
0	126	149
1	216	213
-1	235	234
2	257	266
-2	230	238
3	157	144
-3	171	155
4	84	81
-4	66	64
5	141	133
-5	111	110
6	345	354
-6	327	348
7	99	99
-7	101	111
8	52	43
-8	36	45
9	153	139
-9	174	169
10	127	108
-10	118	92
11	103	101
-11	113	98
13	123	114
-13	134	115
14	121	126
-14	118	118
15	67	58
-15	66	67
16	68	52
-16	67	56
17	45	38
18	85	83
-18	105	97
19	69	53
-19	47	46
-21	44	45
-22	42	40
-25	40	45
H= 9, K= 1		
0	176	217
1	54	115
-1	116	134
2	267	290
-2	318	336
3	51	75
-3	102	101
4	51	82
-4	88	87
5	92	85
-5	52	77
6	281	284
-6	259	268
7	42	34
-7	41	37
8	40	62
-8	73	64
9	127	110
-9	129	126
10	151	181
-10	190	182
11	82	78
-11	66	60
12	60	59
-12	60	60
-14	171	147
-15	35	25
16	36	24
17	51	45
-17	50	49
18	138	127
-18	130	125
-22	56	48
H= 11, K= 1		
0	33	32
1	59	55
-1	58	60
2	235	275
-2	240	275
3	58	90
-3	87	69
4	113	104
-4	113	101
5	69	77
-5	70	65
6	158	194
-6	189	168
7	66	82
-7	53	92
8	50	49
-8	45	47
9	36	29
-9	50	31
10	179	188
-10	155	200
11	53	75
-11	101	76
12	38	42
-12	53	42
13	56	56
-13	77	54
14	136	119
-14	142	115
16	28	35
-16	37	38
-17	36	29
18	80	84
-18	70	62
-19	47	39
-22	82	67
H= 13, K= 1		
0	116	115
1	111	119
-1	118	129
2	137	158
-2	134	167
3	104	115
-3	123	133
4	48	47
-4	35	41
5	83	87
-5	51	87
6	138	131
-6	153	147
7	37	49
-7	36	38
8	40	36
-8	59	44
9	153	130
-9	157	131
10	166	157
-10	169	158
11	54	83
-11	82	65
12	85	63
-12	72	61
13	66	64
-13	84	66
14	114	101
-14	113	96
15	109	93
-15	112	91
-16	36	25
-17	36	39
18	49	49
-18	56	72
-21	32	31
-22	44	47
H= 15, K= 1		
0	51	31
1	52	50
-1	67	67
2	90	105
-2	66	95
3	119	130
-3	118	120
4	108	112
-4	100	104
5	100	117
-5	107	110
6	146	172
-6	144	158
7	130	134
-7	123	121
8	127	135
-8	140	144
9	84	81
-9	81	75
10	35	34
-10	49	50
11	52	85
-11	110	92
13	37	41
14	74	69
-14	72	59
15	85	76
-15	55	74
16	55	50
-16	62	57
17	58	64
-17	57	58
18	52	53
-18	62	53
19	45	49
-19	45	39
-20	27	29
-21	32	33
H= 17, K= 1		
0	178	152
1	82	82
-1	52	52
2	37	34
-2	37	39
3	53	56
-3	65	73
-4	165	177
5	69	66
-5	55	67
6	86	86
-6	81	77
7	53	80
-7	116	98
8	109	111
-8	109	101
9	41	54
-9	59	58
10	51	41
11	74	63
-11	100	74
12	71	71
-12	75	75
13	82	78
-13	64	72
-14	38	28
15	37	31
-15	51	34
16	54	58
-16	58	62
-17	37	29
-19	51	48
-20	27	25
H= 19, K= 1		
0	175	189
1	75	72
-1	87	80
2	25	26
-2	25	29
3	51	47
-3	51	55
4	127	135
-4	116	117
5	58	64
-5	52	56
6	52	49
-6	37	47
-7	26	30
8	106	111
-8	97	100
-9	45	47
11	36	26
-11	36	29
12	121	122
-12	121	117
13	48	41
-13	47	39
15	29	18
-15	40	21
16	45	50
-16	56	52
H= 21, K= 1		
0	119	134
1	23	26
-1	23	31
4	104	106
-4	101	101
6	33	25
-6	23	21
7	33	25
-7	32	29
8	110	107
-8	114	115
11	29	24
-11	36	29
12	102	104
13	36	38
-13	44	41
14	16	5
H= 23, K= 1		
0	67	63
-1	54	41
3	31	25
-3	31	29
4	119	129
-4	119	121
5	80	67
-5	80	70
7	73	60
-7	69	61
8	77	80
-8	80	84
-11	23	33
12	66	52
-12	56	58
-13	42	41
H= 25, K= 1		
0	48	48
1	46	52
-1	60	55
2	49	33
-2	36	38
3	70	67
-3	71	66
4	68	60
-4	67	64
5	51	43
-5	44	38
6	62	55
-6	52	48
7	46	37
-7	41	40
8	54	48
-8	44	45
9	66	62
-9	69	66
H= 0, K= 2		
1	181	172
2	159	171
-2	144	171
3	113	74
-3	109	74
4	52	69
-4	50	69
5	226	208
-5	216	208
6	165	149
-6	166	149
7	154	147
-7	148	147
8	168	166
-8	162	166
9	102	89
-9	55	89
11	53	94
-11	65	94
12	255	264
-12	249	264
-15	40	52
-16	92	78
-18	79	82
-20	46	44
-24	37	57
H= 2, K= 2		
0	245	215
1	226	219
-1	208	222
2	119	90
-2	110	85
3	212	196
-3	202	195
4	383	402
-4	330	351
5	146	126
-5	175	158
6	168	148
-6	159	146
7	64	54
-7	86	77
8	256	230
-8	239	237
9	107	103
-9	97	106
10	45	40
-10	44	40
11	57	93
-11	80	82
12	169	179
-12	150	147
13	109	93
-13	53	79
14	73	66
-14	55	70
-15	41	33
16	149	130
-16	113	110
-19	46	51
-20	80	90
-24	37	34
H= 4, K= 2		
0	81	96
1	122	112
-1	160	152
2	55	37
-2	38	28
3	161	143
-3	162	152
4	257	234
-4	252	237
5	264	261
-5	231	234
6	88	65
-6	54	33
7	149	152
-7	195	190
8	140	119
-8	138	132
9	209	194
-9	209	202
10	36	37
-10	70	55
11	50	87
-11	117	120
12	121	109
-12	81	79
13	78	74
-13	69	67
-14	18	21
15	87	79
-15	101	84
16	53	83
-16	100	96
17	103	98
-17	87	95
-18	66	69
-19	81	81
-20	46	40
-21	45	34
H= 6, K= 2		
0	151	213
1	131	121
-1	137	137
2	115	102
-2	154	144
3	176	172
-3	164	176
4	105	95
-4	67	80
5	212	202
-5	207	213
6	98	95
-6	106	118
7	234	223
-7	187	195
8	80	84
-8	61	67
9	92	63
-9	92	76
10	130	120
-10	95	87
11	149	131
-11	164	148
12	51	84
-12	103	93
13	112	110
-13	52	96
14	66	66
-14	65	85
15	83	73
-15	75	78
-16	66	50
17	99	104
-17	99	98
18	70	53
-18	68	43
-19	47	44
-21	71	58
H= 8, K= 2		
0	80	75
1	98	100
-1	55	59
2	276	261
-2	277	277
3	262	232
-3	222	217
4	74	64
-4	82	64
5	65	66
-5	87	93
6	222	212
-6	196	198
7	127	110
-7	105	101
8	59	43
-8	58	42
9	75	55
-9	66	70
10	240	220
-10	232	219
11	127	115
-11	103	99
13	117	99
-13	125	106
14	154	145
-14	155	147
15	73	87
-15	78	72
16	52	33
-16	25	29
-17	60	42
18	72	71
-18	52	80
-21	43	50
-22	57	61
H= 10, K= 2		
1	35	29
-1	42	43
2	229	259
-2	228	268
3	135	141
-3	133	134
4	76	75
-4	85	81
5	149	130
-5	159	145
6	228	205
-6	213	198
7	69	75
8	73	81
-8	66	70
-9	48	41
10	207	193
-10	225	216
11	52	61
-11	72	66
12	38	31
-12	52	40
13	24	21
-13	38	23
14	146	128
-14	117	109
16	26	29
17	37	28
18	51	59
-18	69	65
-19	47	40
-22	46	49
-23	23	25
H= 12, K= 2		
0	25	28
1	51	103
-1	83	102
2	170	191
-2	166	193
3	181	193
-3	192	198
5	49	55
-5	103	93
6	239	234
-6	226	224
7	90	98
-7	101	92
9	71	73
-9	55	62
10	117	111
-10	121	110
11	102	89
-11	89	89
12	104	82
-12	55	80
13	74	67
-13	71	60
14	107	105
-14	112	109
15	102	105
-15	107	97
16	25	42
-16	53	44
17	67	50
-17	63	52
18	89	97
-18	51	54
H= 14, K= 2		
0	45	47
1	114	125
-1	105	119
2	111	125
-2	147	167
3	96	104
-3	105	122
4	64	55
-4	69	67
5	162	165
-5	155	159
6	105	117
-6	87	87
7	154	155
-7	153	154
8	22	38
-8	35	28
9	78	79
-9	110	99
10	115	101
-10	89	75
11	109	94
-11	127	98
-12	59	37
13	77	60
-13	73	57
14	88	65
-14	70	66
15	98	99
-15	94	43
16	54	38
-16	51	49
-17	46	44
18	43	39
-18	41	42
19	52	48
-19	50	49
-20	21	34
-22	27	39
H= 16, K= 2		
0	53	70
1	121	131
-1	118	125
2	89	97
-2	86	92
3	109	107
-3	119	109
4	85	98
-4	84	85
5	61	73
-5	51	50
6	42	38
-6	29	16
7	74	60
-7	103	54
8	62	50
-8	75	68
9	101	99
-9	109	107
10	75	70
-10	65	77
11	87	80
-11	86	79
12	73	80
-12	92	79
13	65	61
-13	82	73
-14	42	36
15	71	61
-15	82	75
16	38	42
-16	37	36
17	34	35
-17	33	27
-18	30	16
-19	37	43
-20	22	29
H= 18, K= 2		
0	110	111
1	53	65
-1	65	75
2	65	52
-2	93	48
3	54	40
-3	38	40
4	135	149
-4	128	141
5	78	67
-5	77	76
7	69	47
-7	56	41
8	121	121
-8	124	125
-9	65	65
10	40	29
-10	35	29
-11	39	35
12	102	98
-12	98	93
13	37	33
-13	26	19
-14	34	32
15	46	47
-15	45	39
16	65	65
-16	58	63
17	18	24
-17	25	25
H= 20, K= 2		
0	121	124
-1	50	44
-2	35	37
3	50	59
-3	58	62
4	109	106
-4	105	103
5	73	65
-5	71	63
7	61	52
-7	61	54
8	107	103
-8	104	106
9	34	34
-9	34	32
10	33	25
-10	33	28
-11	32	22
12	71	69
-12	73	65
13	29	32
-13	28	28
15	34	31
-15	33	32
16	71	66
-16	72	72
17	29	36
-17	33	31
H= 22, K= 2		
0	104	108
1	47	35
-1	47	42
3	58	58
-3	57	58
4	110	109
-4	111	117
5	56	48
-5	61	53
7	31	33
-7	44	42
8	113	105
-8	58	93
9	51	51
-9	51	47
11	33	29
-11	37	30
12	53	54
-12	46	54
13	31	32
-13	37	33
H= 24, K= 2		
0	67	88
1	64	63
-1	66	54
-2	31	29
3	66	52
-3	43	44
4	76	61
-4	72	58
5	36	33
-5	41	39
6	28	17
-6	12	9
7	51	43
-7	51	43
8	49	39
-8	43	39
9	99	45
-9	98	52
10	30	28
-10	30	29
11	42	42
-11	46	49
H= 26, K= 2		
1	76	67
-1	78	69
2	41	37
-2	29	31
3	43	41
-3	44	47
4	37	38
-4	19	28
5	52	53
-5	53	56
H= 1, K= 3		
1	133	106
-1	156	139
2	67	86
-2	87	91
3	159	161
-3	157	199
4	337	336
-4	342	351
5	127	106
-5	124	119
6	50	57
-6	42	41
7	55	45
-7	100	87
8	270	258
-8	240	235
9	137	136
-9	99	107
10	50	86
-10	87	92
11	50	51
-11	66	80
12	151	200
-12	174	202
13	48	58
-13	66	52
14	59	69
-14	49	64
-15	72	81
-16	108	127
-17	71	68
-18	20	37
-19	32	32
-20	56	62
-24	24	33
H= 3, K= 3		
0	155	174
1	253	237
-1	223	231
2	146	138
-2	130	135
3	256	299
-3	233	296
4	208	202
-4	207	213
5	287	277
-5	276	283
6	62	49
-6	60	45
7	177	164
-7	186	179
8	83	88
-8	63	60
9	166	156
-9	141	143
10	65	58
-10	69	64
11	150	143
-11	135	145
12	147	139
-12	125	136
13	115	114
-13	100	108
14	43	38
15	72	64
-15	61	63
16	55	52
-16	85	96
-17	20	23
-18	20	27
-20	45	57
-23	38	52
H= 5, K= 3		
0	125	177
1	222	211
-1	153	211
2	223	209
-2	187	199
3	356	354
-3	334	370
4	159	149
-4	142	150
5	267	260
-5	238	259
6	133	120
-6	118	116
7	165	157
-7	137	141
8	112	93
-8	119	102
9	176	188
-9	155	174
10	56	88
-10	116	110
11	154	134
-11	154	147
13	121	102
-13	54	50
14	82	78
-14	63	70
15	59	55
-15	64	68
16	21	14
-16	20	17
17	71	78
-17	66	83
-18	47	56
-19	66	72
-20	45	45
H= 7, K= 3		
0	57	116
1	183	205
-1	171	189
2	163	159
-2	139	149
3	168	172
-3	140	155
5	160	135
-5	107	97
6	159	164
-6	149	171
7	124	111
-7	122	120
8	18	28
9	54	105
-9	54	111
10	136	121
-10	123	125
11	131	123
-11	118	118
-12	20	20
13	54	53
-13	54	95
14	104	103
-14	96	88
15	74	75
-15	68	72
-16	21	17
17	51	87
-17	69	80
18	52	47
-18	48	55
-21	30	41
H= 9, K= 3		
0	75	106
1	57	62
-1	77	85
2	141	153
-2	166	152
3	113	106
-3	118	128
5	55	88
-5	52	54
6	153	156
-6	112	135
7	144	124
-7	142	141
8	21	28
-8	20	34
9	78	74
-9	66	56
10	156	185
-10	167	177
11	37	38
-11	35	47
-12	43	37
13	57	50
-13	52	58
14	58	91
-14	50	90
15	56	44
-15	63	60
16	35	41
-16	36	27
17	38	32
-17	21	23
18	74	80
-18	83	83
19	50	42
-19	46	48
-20	43	44
-21	28	18
H= 11, K= 3		
0	36	35
1	105	114
-1	59	58
2	157	154
-2	139	172
3	103	113
-3	116	123
4	68	68
-4	46	46
5	57	89
-5	106	103
6	174	160
-6	146	149
7	81	82
-7	51	77
8	50	79
-8	51	89
9	57	48
-9	53	63
10	180	178
-10	175	186
11	134	127
-11	128	123
12	42	32
-12	39	28
13	61	61
-13	69	62
14	86	51
-14	59	106
15	41	50
-15	23	36
16	40	44
17	28	28
-17	50	28
18	73	80
-18	67	71
-19	~49	42
H= 13, K= 3		
0	37	36
1	166	174
-1	186	152
2	144	166
-2	147	167
3	90	96
-3	84	91
4	42	42
-4	41	41
5	54	57
-5	59	59
6	108	111
-6	107	118
7	53	59
-7	89	81
8	26	37
-8	24	33
9	110	99
-9	52	94
10	50	74
-10	83	66
11	112	98
-11	83	84
12	28	16
-12	26	20
13	65	61
-13	84	77
14	51	92
-14	80	80
15	50	68
-15	54	50
16	19	28
-16	36	28
17	53	49
-17	34	41
18	48	48
-18	44	57
-19	27	33
H= 15, K= 3		
0	47	42
1	102	121
-1	96	110
2	48	46
-2	55	44
3	124	139
-3	119	135
4	83	80
-4	76	78
5	117	120
-5	127	130
6	90	91
-6	53	89
7	122	118
-7	117	117
8	20	37
-8	46	51
9	126	126
-9	116	124
10	71	55
-10	84	76
-11	49	66
12	51	37
-12	35	22
13	36	35
-13	49	48
14	49	40
-14	46	33
15	45	47
-15	61	61
16	29	28
-16	40	31
17	37	47
-17	36	59
-18	32	31
-19	39	50
H= 17, K= 3		
0	54	57
1	129	150
-1	117	132
2	62	51
-2	55	49
3	79	66
-3	84	56
4	69	75
-4	83	89
5	117	128
-5	151	125
7	64	89
-7	63	89
8	84	91
-8	72	77
9	42	52
-9	41	44
-10	41	26
11	73	82
-11	71	83
12	83	79
-12	81	80
13	57	57
-13	54	49
14	26	26
-14	30	28
15	39	48
-15	56	50
16	49	40
-16	43	44
17	34	49
-17	43	52
-18	23	18
H= 19, K= 3		
0	51	57
1	83	75
-1	54	56
2	52	37
-2	37	28
3	65	65
-3	64	61
4	83	86
-4	61	60
5	53	37
-5	45	45
-6	37	26
7	53	61
-7	52	64
8	83	99
-8	90	94
9	68	70
-9	65	64
-10	35	31
11	55	50
-11	49	51
12	80	87
-12	76	84
13	63	65
-13	53	59
14	12	13
15	45	48
-15	44	49
16	40	51
-16	49	51
H= 21, K= 3		
0	119	124
1	59	65
-1	85	65
2	34	40
-2	34	41
3	59	56
-3	46	48
4	107	108
-4	102	106
5	47	49
-5	58	57
6	33	39
-6	47	37
7	40	36
-7	51	45
8	83	82
-8	53	93
9	53	53
-9	62	58
10	21	23
11	45	48
-11	48	48
12	62	67
-12	59	64
13	41	42
-13	40	45
14	14	26
-14	20	33
H= 23, K= 3		
0	63	80
1	43	49
-1	53	48
3	55	60
-3	55	53
4	64	85
-4	75	76
5	75	67
-5	72	69
-6	20	15
7	57	60
-7	65	55
8	66	56
-8	67	62
9	43	44
-9	43	36
-10	22	9
11	28	28
-11	14	20
12	35	44
-12	34	42
H= 25, K= 3		
-1	60	51
3	55	55
-3	56	55
-4	42	36
5	50	60
-5	53	53
-6	26	28
7	51	55
-7	50	56
H= 0, K= 4		
1	131	135
-1	106	135
2	138	109
-2	133	109
3	153	139
-3	152	139
4	209	195
-4	208	195
5	64	55
-5	63	55
6	120	117
-6	112	117
7	126	124
-7	123	124
8	228	224
-8	215	224
9	32	32
-9	44	32
10	131	136
-10	126	136
11	179	175
-11	170	175
-12	146	154
-13	99	99
-14	110	114
-15	20	22
-16	44	46
-17	31	33
-18	45	51
-19	19	16
-20	62	62
-21	35	36
H= 2, K= 4		
0	161	157
1	225	231
-1	228	260
2	56	65
-2	108	110
3	160	142
-3	152	146
4	159	196
-4	167	166
5	206	192
-5	183	180
6	133	120
-6	160	145
7	168	142
-7	177	159
8	105	101
-8	139	143
9	135	125
-9	121	117
10	[illegible]	55

Table 6 (*cont.*)

H= 2, K= 4		
-10	67	72
11	96	92
-11	82	77
12	99	96
-12	96	99
13	106	93
-13	96	94
-14	89	90
-15	61	61
-16	77	85
-17	45	55
-18	32	32
-19	31	37
-20	62	65
-21	41	46
H= 4, K= 4		
0	37	21
1	238	207
-1	169	177
2	63	44
-2	52	44
3	237	232
-3	192	213
4	190	172
-4	178	173
5	273	255
-5	255	257
6	79	62
-6	76	65
7	193	171
-7	182	174
8	73	61
-8	60	49
9	197	164
-9	200	185
10	42	24
-10	38	29
11	95	78
-11	68	76
12	84	79
-12	71	77
13	122	116
-13	105	107
15	69	73
-15	71	71
-16	56	57
-17	92	101
-18	20	18
-19	45	62
-20	30	29
H= 6, K= 4		
1	237	212
-1	206	214
2	149	134
-2	133	150
3	175	176
-3	142	158
4	66	63
-4	63	65
5	167	149
-5	154	161
6	84	68
-6	84	81
7	168	143
-7	145	137
8	41	38
-8	39	35
9	136	112
-9	109	94
10	126	115
-10	117	108
11	153	124
-11	127	121
12	50	39
-12	45	39
13	88	81
-13	65	75
14	73	61
-14	81	78
15	74	79
-15	94	98
16	52	44
-16	47	49
-17	66	69
-18	46	50
-19	63	74
H= 8, K= 4		
0	12	15
1	138	152
-1	125	141
2	60	50
-2	84	81
3	141	128
-3	110	109
4	77	69
-4	63	63
5	82	78
-5	83	95
6	90	77
-6	94	98
7	118	112
-7	122	125
8	48	41
-8	31	34
9	133	130
-9	96	104
10	89	79
-10	82	89
11	135	115
-11	116	107
12	56	54
-12	61	60
13	98	76
-13	79	85
14	79	61
-14	61	60
15	79	75
-15	60	68
16	55	27
-17	47	34
-18	46	54
H= 10, K= 4		
0	87	84
1	121	132
-1	102	111
2	154	180
-2	128	160
3	110	108
-3	98	111
4	98	76
-4	96	102
5	129	105
-5	100	110
6	140	118
-6	107	114
7	96	80
-7	88	82
8	143	132
-8	134	113
9	79	76
-9	51	74
10	137	135
-10	126	141
11	129	119
-11	120	131
12	60	60
-12	54	57
13	61	41
-13	53	52
14	104	92
-14	74	80
15	58	38
-15	36	32
16	56	45
-16	49	50
-17	47	34
-18	45	54
H= 12, K= 4		
0	27	17
1	79	93
-1	85	97
2	126	132
-2	118	117
3	139	157
-3	139	155
4	45	32
-4	61	53
5	144	136
-5	143	144
6	134	123
-6	123	126
7	126	97
-7	104	83
-8	25	47
9	111	93
-9	95	110
10	91	86
-10	57	62
-11	25	31
12	28	25
-12	25	21
13	65	55
-13	56	56
14	89	73
-14	76	74
15	73	75
-15	63	71
16	56	36
-16	34	34
17	52	47
-17	32	58
H= 14, K= 4		
0	39	33
1	125	136
-1	133	144
2	85	86
-2	100	106
3	115	121
-3	113	115
4	42	42
-4	41	41
5	112	114
-5	104	114
6	80	75
-6	77	76
7	125	129
-7	122	134
8	72	64
-8	84	68
9	107	98
-9	87	86
10	56	57
-10	52	53
11	81	76
-11	65	75
12	41	41
-12	37	43
13	58	50
-13	52	56
14	54	51
-14	68	64
15	61	66
-15	45	56
H= 16, K= 4		
0	27	32
1	112	116
-1	107	101
2	28	16
-2	27	18
3	110	119
-3	115	121
4	58	59
-4	57	54
5	66	69
-5	64	59
-6	29	36
7	68	76
-7	66	76
-8	30	24
9	88	88
-9	75	82
11	105	108
-11	86	96
12	43	36
-12	29	43
13	42	50
-13	55	57
14	27	18
-14	16	17
15	44	56
-15	48	61
16	32	36
-16	31	37
17	35	48
-17	33	35
H= 18, K= 4		
1	85	100
-1	77	84
2	53	56
-2	65	69
3	74	81
-3	77	75
4	66	66
-4	65	65
5	82	85
-5	76	74
6	17	11
7	66	77
-7	76	76
8	73	77
-8	75	83
9	66	71
-9	64	69
10	37	44
-10	44	39
11	51	60
-11	61	68
12	35	41
-12	33	38
13	65	73
-13	54	70
14	21	28
-14	29	35
15	27	39
-15	32	37
-16	23	26
-17	26	45
H= 20, K= 4		
0	105	113
1	52	53
-1	62	61
2	37	49
-2	37	41
3	62	67
-3	52	61
4	69	71
-4	71	73
5	82	83
-5	81	90
6	44	46
-6	49	50
7	65	65
-7	72	70
8	70	71
-8	71	70
9	63	53
-9	53	46
10	40	35
-10	39	39
11	31	27
-11	30	20
12	62	68
-12	62	71
13	26	26
-13	25	33
14	23	25
-14	15	17
H= 22, K= 4		
2	31	32
-2	31	24
3	54	59
-3	56	64
4	68	64
-4	73	77
5	58	59
-5	67	63
6	29	28
-6	36	36
7	41	45
-7	40	44
8	61	62
-8	55	53
9	52	54
-9	45	50
10	24	25
-10	23	31
11	30	31
-11	30	28
12	31	36
-12	31	43
H= 24, K= 4		
1	75	81
-1	64	73
3	78	67
-3	61	56
4	45	38
-4	42	35
5	48	46
-5	43	49
7	45	53
-7	32	40
-8	38	37
H= 1, K= 5		
1	48	51
-1	87	90
2	137	130
-2	108	106
3	110	112
-3	117	116
4	141	124
-4	180	164
5	102	90
-5	109	92
6	116	110
-6	131	128
7	155	149
-7	142	144
8	127	107
-8	78	68
9	104	83
-9	88	79
10	80	66
-10	84	79
11	75	65
-11	49	39
12	86	72
-12	63	60
13	93	89
-13	81	86
-14	78	89
-15	70	83
-16	41	35
-17	58	72
-18	28	36
H= 3, K= 5		
0	110	98
1	216	206
-1	155	183
2	102	97
-2	84	88
3	127	119
-3	117	122
4	96	97
-4	93	108
5	142	122
-5	139	121
6	114	98
-6	117	105
7	140	119
-7	125	116
8	110	84
-8	100	83
9	111	94
-9	75	67
10	83	57
-10	86	64
11	129	117
-11	131	132
12	92	90
-12	106	106
13	124	106
-13	127	126
-14	16	16
15	56	52
-15	41	46
-16	59	67
-17	50	54
-18	41	39
H= 5, K= 5		
0	35	26
1	173	158
-1	112	132
2	111	90
-2	92	91
3	193	177
-3	162	188
4	70	62
-4	68	64
5	138	135
-5	142	150
6	75	60
-6	74	63
7	162	138
-7	134	127
8	87	60
-8	84	58
9	200	176
-9	182	169
10	44	25
-10	40	20
11	86	70
-11	85	69
12	66	32
-12	41	29
13	106	78
-13	73	72
14	58	53
-14	42	47
15	83	83
-15	60	71
-16	17	31
-17	51	51
-19	48	59
H= 7, K= 5		
0	56	44
1	175	182
-1	165	192
2	123	91
-2	86	76
3	182	144
-3	122	128
4	116	101
-4	91	104
5	154	138
-5	121	135
6	35	33
-6	17	25
7	141	118
-7	122	122
8	54	51
-8	50	49
9	140	120
-9	127	130
10	25	28
-10	48	33
11	115	92
-11	79	80
12	52	34
-12	55	48
13	51	49
-13	45	31
14	81	71
-14	63	65
15	124	102
-15	99	105
16	67	61
-16	61	65
17	48	48
-17	42	47
-19	38	36
H= 9, K= 5		
0	86	95
1	85	98
-1	98	114
2	101	96
-2	109	109
3	114	84
-3	80	73
4	133	108
-4	101	102
5	160	127
-5	146	143
6	88	69
-6	72	51
7	146	119
-7	113	116
8	166	145
-8	149	150
9	90	78
-9	74	71
10	117	90
-10	87	85
11	110	81
-11	70	63
12	98	75
-12	59	72
13	113	78
-13	82	93
14	77	52
-14	60	62
15	52	58
-15	45	59
16	50	50
-16	43	51
17	48	44
-17	41	45
18	45	38
-18	39	35
-19	25	40
-20	33	49
-21	13	10
-22	30	39
H= 11, K= 5		
0	135	151
1	127	133
-1	101	115
2	93	103
-2	98	104
3	41	48
-3	57	60
4	75	67
-4	43	34
5	77	65
-5	59	61
6	118	92
-6	103	107
7	84	64
-7	51	48
8	108	87
-8	104	112
9	103	80
-9	90	86
10	103	79
-10	73	67
11	119	92
-11	97	100
12	85	71
-12	74	63
13	67	55
-13	49	52
14	56	33
-14	47	46
15	53	53
-15	55	63
16	62	54
-16	43	38
18	75	62
-18	52	59
-19	40	46
H= 13, K= 5		
0	59	54
1	131	142
-1	120	140
2	87	98
-2	76	76
3	97	106
-3	88	103
4	94	84
-4	100	100
5	115	114
-5	83	91
6	91	81
-6	87	91
7	120	120
-7	120	127
8	28	42
-8	33	20
9	105	98
-9	84	87
10	65	42
-10	63	53
11	104	76
-11	89	78
12	41	41
-12	36	43
13	83	73
-13	68	74
14	65	54
-14	45	49
15	54	39
-15	41	37
16	42	31
-16	37	42
17	44	35
-17	33	32
18	31	21
-18	28	23
-19	33	42
H= 15, K= 5		
1	101	115
-1	94	107
3	96	107
-3	90	103
5	104	111
-5	124	134
-6	21	22
7	113	112
-7	109	117
9	90	83
-9	57	69
10	19	23
-10	18	24
11	51	59
-11	63	65
12	28	25
-12	22	28
13	63	66
-13	51	57
15	74	64
-15	46	59
17	52	58
-17	42	55
H= 17, K= 5		
0	64	60
-1	64	61
2	40	49
-2	40	37
3	90	94
-3	85	83
4	58	34
-4	40	35
5	91	80
-5	89	84
6	77	73
-6	68	70
7	82	83
-7	68	68
8	58	59
-8	40	48
9	40	42
-9	39	43
10	28	20
-10	27	26
11	72	69
-11	75	68
12	16	15
-12	38	25
13	46	54
-13	51	56
14	31	27
-14	29	20
15	39	39
-15	37	45
16	24	19
-17	34	56
H= 19, K= 5		
0	63	58
1	73	72
-1	73	75
2	81	72
-2	73	74
3	89	76
-3	80	86
4	72	56
-4	72	67
5	57	49
-5	43	40
6	39	28
-6	55	47
7	49	54
-7	42	49
8	69	62
-8	53	62
9	74	75
-9	58	69
10	64	60
-10	68	70
11	48	48
-11	41	39
12	28	26
-12	33	27
13	35	37
-13	42	47
14	21	38
-14	25	33
H= 21, K= 5		
0	31	26
1	68	71
-1	68	64
2	43	36
-2	43	46
3	53	43
-3	37	34
4	60	61
-4	52	53
5	51	53
-5	41	47
6	35	34
-6	35	33
7	28	28
-7	39	37
8	38	34
-8	46	44
9	48	46
-9	50	49
10	33	39
-10	27	28
11	25	34
-11	35	38
12	36	34
-12	28	30
H= 23, K= 5		
0	33	38
1	33	40
-1	33	42
2	23	21
-2	23	27
3	54	62
-3	53	60
4	22	24
-4	15	17
5	47	58
-5	52	54
6	40	40
-6	34	40
7	41	48
-7	44	48
8	22	19
-8	26	30
H= 0, K= 6		
1	154	182
-1	147	182
2	203	186
-2	188	186
3	108	106
-3	103	106
4	104	99
-4	93	99
5	78	66
-5	81	66
6	100	102
-6	94	102
7	90	78
-7	77	78
8	53	44
-8	43	44
9	122	104
-9	110	104
-10	127	122
-11	41	43
-12	42	44
-13	88	98
-14	55	52
-15	45	30
-16	41	29
-17	45	39
-18	27	29
-20	16	17
H= 2, K= 6		
0	74	70
1	117	116
-1	101	110
2	142	131
-2	146	137
3	130	111
-3	127	117
4	86	80
-4	61	60
5	181	152
-5	139	119
6	113	104
-6	112	114
7	130	108
-7	131	124
8	77	80
-8	74	86
9	143	112
-9	136	122
10	132	117
-10	92	99
11	110	98
-11	84	85
12	68	67
-12	43	49
-13	53	49
-14	76	80
-15	32	51
-16	45	42
-17	60	72
H= 4, K= 6		
1	159	136
-1	117	124
3	150	125
-3	124	111
4	58	41
-4	52	41
5	135	110
-5	126	117
6	145	124
-6	123	117
7	160	136
-7	137	131
9	100	79
-9	105	101
10	62	49
-10	79	68
11	96	74
-11	97	94
12	52	44
-12	45	42
13	83	87
-13	80	85
-14	20	17
-15	76	86
-16	32	23
-17	49	51
-18	38	43
H= 6, K= 6		
0	78	79
1	176	157
-1	159	177
3	69	41
-3	84	78
4	47	44
-4	24	27
5	113	97
-5	112	105
6	57	28
-6	44	32
7	181	158
-7	156	157
-8	33	31
9	144	113
-9	103	99
10	74	58
-10	67	56
11	122	105
-11	81	85
12	57	50
-12	21	32
13	126	117
-13	109	121
15	60	70
-15	51	73
-17	40	46
-18	18	22
-19	43	61
H= 8, K= 6		
0	150	178
1	104	135
-1	114	131
-2	16	11
3	138	113
-3	107	110
4	120	94
-4	91	90
5	137	122
-5	117	119
6	131	107
-6	107	107
7	112	81
-7	95	91
8	114	93
-8	89	88
9	124	97
-9	91	90
10	47	40
-10	48	34
11	87	73
-11	76	69
12	126	117
-12	98	114
13	76	47
-13	22	34
14	41	23
-14	16	30
15	56	46
-16	15	12
H= 10, K= 6		
0	91	100
1	124	132
-1	111	122
2	82	79
-2	66	74
3	125	117
-3	96	98
4	119	87
-4	100	102
5	109	83
-5	77	79
-6	57	56
7	66	46
-7	80	70
8	138	104
-8	98	94
9	64	47
-9	62	62
10	50	35
-10	40	47
11	103	79
-11	76	78
12	66	64
-12	45	61
13	35	39
14	53	45
-14	39	44
15	56	57
-15	44	52
H= 12, K= 6		
0	55	49
1	43	43
2	63	63
-2	43	65
3	103	107
-3	100	104
4	129	135
-4	117	136
5	102	101
-5	91	88
6	67	59
-6	72	63
7	136	110
-7	109	103
8	88	75
-8	77	86
9	96	67
-9	58	66
10	74	68
-10	52	64
11	67	46
-11	51	54
12	29	24
-12	33	37
13	63	48
-13	48	33
14	25	17
-14	16	13
15	60	57
-15	48	61
16	64	60
-16	55	61
-17	30	20
-19	22	36
H= 14, K= 6		
0	41	42
1	84	85
-1	103	103
3	102	97
-3	103	101
4	54	54
-4	45	45
5	48	59
-5	50	67
-6	21	19
7	70	69
-7	58	59
-8	37	44
9	102	86
-9	83	81
11	71	65
-11	57	58
12	34	31
-12	31	30
13	45	51
-13	41	58
14	18	26
-14	17	26
15	64	64
-15	59	69
-16	13	13
-17	35	53
H= 16, K= 6		
0	41	46
1	64	[illegible]
-1	88	85
2	55	48
-2	36	49
3	73	74
-3	78	83
-4	29	31
5	74	83
-5	85	83
7	84	84
-7	83	92
9	73	81
-9	70	81
10	18	36
-10	39	34
11	63	68
-11	65	69
12	26	34
-12	35	28
13	49	59
-13	54	59
-14	12	23
-15	27	37
H= 18, K= 6		
-1	65	71
-2	84	76
3	75	76
-3	64	63
5	64	64
-5	51	59
6	52	57
-6	39	49
7	51	51
-7	43	50
8	15	19
-8	10	19
9	28	34
-9	55	54
10	40	43
-10	34	43
11	33	40
-11	44	42
12	12	17
-12	8	13
13	48	61
-13	46	56
-14	26	41
H= 20, K= 6		
5	61	56
-5	52	54
6	69	79
-6	65	77
7	45	44
-7	39	45
8	19	25
-8	20	27
9	40	46
-9	24	37
10	28	31
-10	25	31
-11	18	21
H= 22, K= 6		
-4	31	35
-5	47	46
-6	27	41
-7	28	44

the density from 2·05 to about 1·93 and thus this result is in accord with the Fourier syntheses. The crystal had become slightly yellow during the later stages of irradiation, although the cell dimensions did not appear to change.

Note added in proof: – Haschemeyer & Sobell (1964) have recently reported the first observation of the *syn* conformation for the glycosidic torsion angle in a *β*-nucleoside, +138° for deoxyguanosine in crystals of the 1:1 complex formed by this molecule with 5-bromodeoxycytidine. The sugar is in what we have termed above the *gg* conformation, but φ_{OC} is only 32°, smaller than any value in Table 3; O(5′) has thus moved slightly away from the base to minimize repulsion, but its position is stabilized by a presumed hydrogen bond from N(3′), 2·82Å away.

We are indebted to Dr A. M. Michelson for the sample of barium uridine phosphate, to Dr Malcolm Barlow who made a preliminary study of the crystals, to Dr Håkon Hope for his generous counsel and advice, to Professor C. S. Foote for helpful discussions, to Maryellin Reinecke for preparing the illustrations, and to Dr M. Sundaralingam for sending us his unpublished manuscript. The investigation would not have been possible without the cooperation and equipment provided to us by the UCLA Computing Facility and Health Sciences Computing Facility, and the support of the U. S. Public Health Service.

References

AINSWORTH, J. & KARLE, J. (1952). *J. Chem. Phys.* **20**, 425.
ALVER, E. & FURBERG, S. (1959). *Acta Chem. Scand.* **13**, 910.

BASTIANSEN, O. (1949). *Acta Chem. Scand.* **3**, 415.
BEEVERS, C. A. & COCHRAN, W. (1947). *Proc. Roy. Soc.* A **190**, 257.
BOLTON, W. (1963). *Acta Cryst.* **16**, 166.
BRINTZINGER, H. (1961). *Helv. Chim. Acta,* **44**, 935, 1199.
BROWN, G. M. & LEVY, H. A. (1963). *Science,* **141**, 921.
CLARK, J. R. (1963). *Rev. Pure Appl. Chem.* **13**, 50.
DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
DONOHUE, J. & TRUEBLOOD, K. N. (1960). *J. Mol. Biol.* **2**, 363.
FERRIER, W. G. (1963). *Acta Cryst.* **16**, 1023.
FOSS, O., FURBERG, S. & ZACHARIASEN, H. (1954). *Acta Chem. Scand.* **8**, 459.
FURBERG, S. (1960). *Acta Chem. Scand.* **14**, 189.
FURBERG, S. & MOSTAD, A. (1962). *Acta Chem. Scand.* **16**, 1627.
GERDIL, R. (1961). *Acta Cryst.* **14**, 333.
HARRIS, D. R. & MACINTYRE, W. M. (1964). *Biophys. J.* **4**, 203.
HASCHEMEYER, A. & SOBELL, H. (1964). *Nature, Lond.* **202**, 969.
HODGKIN, D. C., LINDSEY, J., SPARKS, R. A., TRUEBLOOD, K. N. & WHITE, J. G. (1962). *Proc. Roy. Soc.* A **266**, 494.
HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JACOBSON, R. A., WUNDERLICH, J. A. & LIPSCOMB, W. N. (1961). *Acta Cryst.* **14**, 598.
KIRBY, K. J. (1957). *Biochem. J.* **66**, 495.
KIRBY, K. J. (1958). *Biochem. J.* **70**, 260.
KRAUT, J. (1961). *Acta Cryst.* **14**, 1146.
KRAUT, J. & JENSEN, L. H. (1963). *Acta Cryst.* **16**, 79.
McDONALD, T. R. R. & BEEVERS, C. A. (1952). *Acta Cryst.* **5**, 654.
MATHEWS, F. S. & RICH, A. (1964). *J. Mol. Biol.* **8**, 89.
NARDELLI, M. & FAVA, G. (1962). *Acta Cryst.* **15**, 477.
PARRY, G. S. (1954). *Acta Cryst.* **7**, 313.
PATTERSON, A. L. (1963). *Acta Cryst.* **16**, 1255.
PEERDEMAN, A. F. & BIJVOET, J. M. (1956). *Acta Cryst.* **9**, 1012.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
SHEFTER, E., BARLOW, M., SPARKS, R. & TRUEBLOOD, K. N. (1964). *J. Amer. Chem. Soc.* **86**, 1872.
SPENCER, M. (1959). *Acta Cryst.* **12**, 59.
SUNDARALINGAM, M. (1964). Private communication.
SUNDARALINGAM, M. & JENSEN, L. H. (1964). Private communication.
SUTOR, D. J. (1963). *J. Chem. Soc.* p. 1105.
TEMPLETON, D. (1960). *Acta Cryst.* **13**, 684.
THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.
TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.
TRUEBLOOD, K. N., HORN, P. & LUZZATI, V. (1961). *Acta Cryst.* **14**, 965.
WATSON, D. G., SUTOR, D. J. & TOLLIN, P. (1963). Private communication to M. Sundaralingam.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1965). **18**, 1077

On weights for a least-squares refinement.

By A. DE VRIES. *Laboratorium voor Kristalchemie der Rijksuniversiteit, Utrecht, The Netherlands.*

(*Received* 12 *September* 1964)

The determination of the probable errors

The object of a least-squares refinement is the minimization of a quantity such as

$$\Sigma w(hkl)\{F_{\rm obs}(hkl)-F_{\rm calc}(hkl)\}^2$$

in which the weight $w(hkl)$ of each term should be taken inversely proportional to the square of the probable error of the corresponding $F_{\rm obs}$ (see *e.g.* Lipson & Cochran, 1957); $F_{\rm obs}$ and $F_{\rm calc}$ stand here and in the following for their moduli. The essential problem in the determination of weights is therefore how to get an estimate of the probable errors in the measurements. There are three basically different methods of doing this, which are briefly discussed.

One way is to determine experimentally the probable error in $F_{\rm obs}$ by repeated measurements. This determination is complicated, however, by the presence of various kinds of systematic error.

Another method is to calculate the probable error in $F_{\rm obs}$ on the basis of theoretical considerations (*e.g.* Evans, 1961). Here the systematic errors constitute an even larger problem.

The third method is to refine the structure first, using some arbitrary weighting scheme (*e.g.* the same weight for all reflexions), and next to take $F_{\rm obs}-F_{\rm calc}$ as a measure for the error in $F_{\rm obs}$.

None of these methods is quite correct. The first two for the reason that the weights as defined above are generally not those one really wants, for the deviations in $F_{\rm calc}$ due to approximations in the model (*e.g.* the omission of hydrogen atoms or the use of incorrect atomic scattering factors) should also be taken into account for the calculation of the weights (Kroon, 1962). The third method is not quite correct because errors in $F_{\rm calc}$ due to incorrect parameter values should not be included in the calculation of the weights,