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# The Crystal Structure of Cytosine*

By David L. Barker† and Richard E. Marsh

*Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.*

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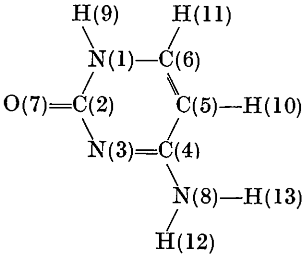
The crystal structure of the pyrimidine cytosine, $C_4H_5N_3O$, has been determined and refined by analysis of complete three-dimensional diffraction data from copper X-radiation. The crystals are orthorhombic with space group $P2_12_12_1$; the unit-cell dimensions are $a = 13{\cdot}041$, $b = 9{\cdot}494$, $c = 3{\cdot}815$ Å. Refinement of the positional parameters for all 13 atoms and of the individual anisotropic temperature factors for the eight heavier atoms was by the method of least squares. For 608 observed reflections of non-zero weight, the final $R$ index is 0·061.

The planar molecule exists in the amino form with a hydrogen atom bonded to N(1) and none to N(3). The amino nitrogen atom participates in two hydrogen bonds to carbonyl oxygen atoms of other molecules; these bonds have relatively long lengths of 2·98 and 3·03 Å. In addition, N(1) forms a hydrogen bond to N(3) of a neighboring molecule at a distance of 2·84 Å.

## Introduction

The determination of the crystal structure of anhydrous cytosine (I) was undertaken as part of a program of research on the structures of compounds related to nucleic acids. Particular interest in cytosine stems from the discovery (Hoogsteen, 1959, 1963) that crystals composed of an equimolar mixture of 1-methylthymine and 9-methyladenine exhibit hydrogen-bond pairing differing from that proposed by Watson & Crick (1953) for deoxyribonucleic acid. A similar pairing between cytosine and guanine, the other pair of complementary bases in deoxyribonucleic acid, would be possible only if there exists a tautomerism which places a proton on either N(3) of cytosine or on N(7) of guanine. More recently, Marsh, Bierstedt & Eichhorn (1962) found that crystals of cytosine-5-acetic acid do indeed contain such a tautomer; in addition, Langridge & Rich (1963) have derived a structure for one form of poly-cytidylic acid which requires N(3) to be protonated one-half the time. It seemed important, then, to examine crystals of cytosine itself. Not unexpectedly, we have found the molecule to exist in the normal form (I).



(I)

Recently, Jeffrey & Kinoshita (1963) carried out a careful determination of the crystal structure of cytosine monohydrate, and we shall take this opportunity to compare the geometries and the patterns of thermal motions of the cytosine molecule in the two structures.

## Experimental

Anhydrous crystals of cytosine were obtained from saturated methanol solutions allowed to evaporate at room temperature. (The compound crystallizes as the monohydrate if small amounts of water are present in the solution.) The crystals are generally needles elongated along $c$; they are stable for several months under atmospheric conditions.

Complete intensity data from Cu $K\alpha$ radiation were collected by the multi-film equi-inclination Weissenberg technique. Of the two crystals used for this work, one was a thin needle from which layer lines 0 to 3 about $c$ were recorded and the other was of approximately equal dimensions in the $a$ and $c$ directions from which layer lines 0 to 8 about $b$ were recorded. The intensities were estimated visually and corrected for Lorentz and polarization factors; no absorption correction seemed necessary. Of the 649 independent reflections within the effective copper sphere ($\sin\theta = 0{\cdot}98$), 613 were observed. All reflections were put on a single scale by use of the 454 reflections which were measured about both $b$ and $c$. These 454 reflections also served as a basis for an estimation of the quality of the observed data. Using the procedure suggested by Ibers (1956), we found that the average standard deviation of a measurement of $F^2$ could be approximated by the expression

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† Present address: Graduate Dept. of Biochemistry, Brandeis University, Waltham, Massachusetts, U.S.A.

$$\sigma(F^2)=0{\cdot}145(F^2+1)$$

where the $F^2$'s are on the final absolute scale. This relationship was the basis of the weighting scheme used in the final least-squares refinement cycles.

The systematic absence of the odd orders of $h00$, $0k0$, and $00l$ determined the space group as $P2_12_12_1$ ($D_2^4$). The unit-cell dimensions (Table 1) were obtained from least-squares analyses of Straumanis-type rotation photographs about $b$ and $c$. Twenty-one $h0l$ and nineteen $hk0$ reflections were indexed by comparison with the corresponding Weissenberg photographs. Their measured values of $\sin^2\theta$, as determined from either Cu $K\alpha_1$ ($\lambda=1{\cdot}54050$) or Cu $K\alpha_2$ ($\lambda=1{\cdot}54434$), were used as input for a least-squares determination of the three cell parameters. The calculations were made by hand and also on a Burrough's 220 computer, with a program developed by Dr Noel Jones. The output cell dimensions and their estimated standard deviations are listed in Table 1. The density calculated on the basis of four molecules per unit cell is 1·562 g.cm$^{-3}$. (The measured and calculated densities of cytosine monohydrate (Jeffrey & Kinoshita, 1963) are 1·478 and 1·473 g.cm$^{-3}$.)

Table 1. *Unit-cell dimensions of anhydrous cytosine*

Orthorhombic; space group $P2_12_12_1$

$a = 13{\cdot}041 \pm 0{\cdot}002$ Å
$b = 9{\cdot}494 \pm 0{\cdot}001$
$c = 3{\cdot}815 \pm 0{\cdot}001$

## Determination of the structure

A trial structure was developed from considerations of packing and hydrogen bonding, with the assumption that the molecule is in the amino form and noting that the short $c$ axis prevents superposition of atoms in the (001) projection. This initial arrangement was confirmed by an electron density projection on (001) and by subsequent two-dimensional refinement by Fourier and least-squares methods. All calculations were carried out on a Burrough's 220 computer, with a Fourier program developed by Dr K. Hoogsteen and a structure-factor least-squares program developed by Dr A. Hybl. The $R$ index for the $hk0$ data fell gradually from an initial value of 0·50 to 0·13, at which point a difference Fourier synthesis was calculated in an attempt to locate the hydrogen atoms. This synthesis showed, in addition to peaks in the expected positions near C(5), C(6), and N(8) (two peaks), a fifth peak clearly indicating a hydrogen atom bonded to N(1); there was no indication of a proton bonded to N(3). Only one spurious peak of any consequence was present, near N(3) on the N(3)–C(4) bond. With the hydrogen positions included, four least-squares cycles, in which anisotropic temperature factors for the heavy atoms were adjusted, reduced $R$ to 0·089 and completed the two-dimensional refinement. The final electron density projection onto (001) is shown in Fig. 1.

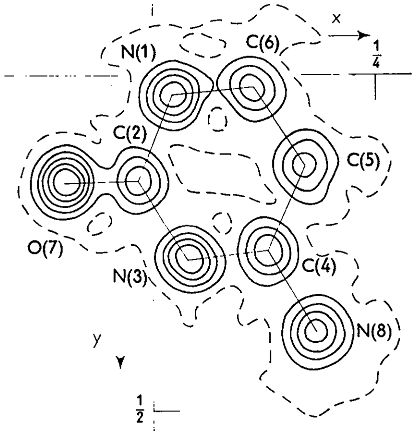

Fig. 1. The electron density projected onto (001). Contours are at intervals of 2 e.Å$^{-2}$ beginning with 1 e.Å$^{-2}$ (dashed).

Approximate $z$ parameters were obtained from a geometrical construction utilizing predicted dimensions of the molecule and its observed projection onto (001). These parameters were improved by an electron density projection onto (010) and three-dimensional refinement was begun. An initial weighting function,

$$\sqrt{w}=1/(1+F_o)\,,$$

was chosen somewhat arbitrarily. (Throughout the three-dimensional refinement, an additional external weight of two was applied to the 454 reflections which were observed about two axes. The quantity minimized was $\Sigma w(F_o^2-F_c^2)^2$. The normal equations were diagonal with respect to the positional parameters, but included cross terms relating the different anisotropic temperature factors of the same atom.) The first structure-factor calculation yielded an $R$ index of 0·27; this was reduced to 0·22 after three cycles of least-squares refinement, during which heavy-atom positional and anisotropic temperature factor parameters were adjusted but the hydrogen atoms were kept stationary. At this point the weighting scheme was changed to $\sqrt{w}=0{\cdot}1+\sin\theta$. After six least-squares cycles $R$ dropped to 0·135 and the weighting scheme was then changed back to the original function. Nine more least-squares cycles resulted in an $R$ value of 0·070. The hydrogen atom positional parameters were permitted to shift during the last three of these, when $R$ had fallen to 0·085.

The final weighting function, $\sqrt{w}=1/[0{\cdot}145(1+F^2)]$ (see *Experimental*), was then adopted, and eight least-squares cycles, during which all the positional parameters and the anisotropic temperature parameters of the heavy atoms were allowed to shift,

Table 2. *The final atomic parameters and their standard deviations*

The heavy atom values have been multiplied by $10^4$. The temperature factors are in the form $T_i = \exp(-\alpha_i h^2 - \beta_i k^2 - \gamma_i l^2 - \delta_i hk - \varepsilon_i hl - \eta_i kl)$. The hydrogen parameters have been multiplied by $10^3$. Each hydrogen was assigned an isotropic $B$ value of 2·5

| Atom | $x(\sigma_x)$ | $y(\sigma_y)$ | $z(\sigma_z)$ | $\alpha(\sigma_\alpha)$ | $\beta(\sigma_\beta)$ | $\gamma(\sigma_\gamma)$ | $\delta(\sigma_\delta)$ | $\varepsilon(\sigma_\varepsilon)$ | $\eta(\sigma_\eta)$ |
|---|---|---|---|---|---|---|---|---|---|
| N(1) | 225(1) | 292(2) | 4402(6) | 31(1) | 50(2) | 520(15) | −4(2) | 3(7) | −4(10) |
| C(2) | −163(2) | 1559(2) | 3272(6) | 30(1) | 55(3) | 422(18) | 1(3) | 27(6) | −13(11) |
| N(3) | 401(1) | 2745(2) | 3875(5) | 27(1) | 45(2) | 504(14) | 6(2) | 6(6) | 1(10) |
| C(4) | 1310(2) | 2647(3) | 5480(7) | 28(1) | 66(3) | 441(16) | 0(2) | 8(7) | 0(11) |
| C(5) | 1707(2) | 1335(3) | 6675(8) | 31(1) | 77(3) | 533(19) | 15(3) | −41(8) | 28(13) |
| C(6) | 1138(2) | 181(3) | 6085(7) | 39(1) | 60(3) | 476(19) | 20(3) | 18(9) | 7(12) |
| O(7) | −993(1) | 1593(2) | 1717(6) | 27(1) | 69(2) | 679(16) | −2(2) | −58(5) | 13(10) |
| N(8) | 1844(2) | 3823(2) | 5978(7) | 35(1) | 63(2) | 747(20) | −18(3) | −76(9) | −3(12) |
| H(9) | −10(2) | −50(4) | 392(10) | | | | | | |
| H(10) | 226(3) | 126(4) | 797(12) | | | | | | |
| H(11) | 133(3) | −76(4) | 711(11) | | | | | | |
| H(12) | 160(3) | 466(4) | 549(13) | | | | | | |
| H(13) | 247(3) | 384(4) | 669(10) | | | | | | |

completed the refinement. The final $R$ index for the 608 observed reflections of non-zero weight was 0·061.

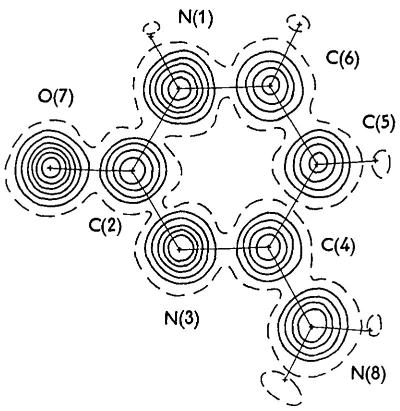

Fig. 2. The electron density in the best plane of the heavy atoms. Contours are at intervals of 2 e.Å$^{-3}$ beginning with 1 e.Å$^{-3}$ (dashed).

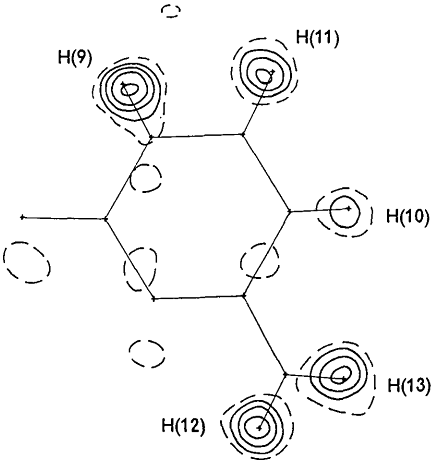

Fig. 3. The final difference map in the plane of the heavy atoms, in which the hydrogen contributions were omitted from the $F_c$'s. Contours are at intervals of 0·1 e.Å$^{-3}$ beginning with 0·2 e.Å$^{-3}$ (dashed). Crosses indicate the final least-squares positions of the atoms.

In the last cycle, no parameter shift exceeded one-fourth of its standard deviation. Unobserved reflections were not included in the $R$ index, and were included in the least-squares refinement only if the calculated structure factor exceeded the minimum observable value. The final atomic parameters and their standard deviations are given in Table 2. Observed and calculated structure factors are given in Table 3.

At the conclusion of the refinement an electron density map and a difference map, each in the plane of the molecule, were calculated. These are shown in Figs. 2 and 3.

## Accuracy of the results

The final value of the quantity $(\Sigma w(\Delta F^2)^2/(m-s))^{\frac{1}{2}}$ — the standard deviation of an observation of unit weight — is 1·5. The standard deviations in the positional parameters (Table 2) were calculated from the sum of the residuals and the diagonal terms of the least-squares normal equations. The heavy-atom positional parameters show an average standard deviation of about 0·002 Å, leading to a standard deviation in interatomic distance of about 0·003 Å and a limit of error (chosen as three times the standard deviation) of 0·009 Å. The limit of error in a bond angle is about 0·6°. For bonds involving hydrogen atoms, the limits of error are about 0·12 Å in bond length and 6° in bond angle.

The standard deviations of the temperature-factor parameters of the heavy atoms were calculated from the diagonal coefficients of the inverse matrices of the normal equations and include interactions among the six temperature parameters of the same atom.

## Discussion of the structure

### *The intermolecular environment*

The structure of anhydrous cytosine as viewed down the $c$ axis is shown in Fig. 4. Hydrogen bonds are formed by all three available protons — two from the

Table 3. *Observed and calculated structure factors*

Within each group the columns contain the values of $h$, $10F_o$, $|10F_c|$, $10A_c$, and $10B_c$
Reflections designated by an asterisk were omitted from the least-squares and $R$ index calculations

| | | | | |
|---|---|---|---|---|
| | | h00 | | |
| 0 | --- | 2323 | 2323 | 0 |
| 2 | 352* | 449 | 449 | 0 |
| 4 | 141 | 137 | -137 | 0 |
| 6 | 268 | 263 | 263 | 0 |
| 8 | 132 | 104 | 104 | 0 |
| 10 | 105 | 108 | 108 | 0 |
| 12 | 31 | 33 | -33 | 0 |
| 14 | 164 | 155 | -155 | 0 |
| 16 | 16 | 17 | -17 | 0 |
| | | h10 | | |
| 1 | 17 | 10 | 0 | -10 |
| 2 | 336 | 345 | -345 | 0 |
| 3 | 97 | 94 | 0 | 94 |
| 4 | 249 | 256 | 256 | 0 |
| 5 | 23 | 19 | 0 | -19 |
| 6 | 170 | 164 | -164 | 0 |
| 7 | 7 | 7 | 0 | 7 |
| 8 | 241 | 237 | -237 | 0 |
| 9 | 123 | 119 | 0 | 119 |
| 10 | <10 | 0 | 0 | 0 |
| 11 | 28 | 24 | 0 | 24 |
| 12 | 49 | 49 | 49 | 0 |
| 13 | <10 | 1 | 0 | 2 |
| 14 | 99 | 95 | 95 | 0 |
| 15 | <9 | 4 | 0 | 4 |
| 16 | 39 | 39 | 39 | 0 |
| | | h20 | | |
| 0 | 146 | 123 | -123 | 0 |
| 1 | 351 | 367 | 0 | 367 |
| 2 | 51 | 45 | -45 | 0 |
| 3 | 133 | 134 | 0 | 134 |
| 4 | 86 | 76 | 76 | 0 |
| 5 | 138 | 117 | 0 | -117 |
| 6 | 65 | 57 | 57 | 0 |
| 7 | 85 | 78 | 0 | 79 |
| 8 | 42 | 37 | 36 | 0 |
| 9 | 128 | 127 | 0 | 127 |
| 10 | 69 | 70 | 70 | 0 |
| 11 | 79 | 83 | 0 | 83 |
| 12 | 49 | 46 | 46 | 0 |
| 13 | 38 | 41 | 0 | 41 |
| 14 | <17 | 4 | -4 | 0 |
| 15 | 66 | 73 | 0 | -73 |
| 16 | <11 | 2 | 2 | 0 |
| | | h30 | | |
| 1 | 299 | 307 | 0 | 307 |
| 2 | <12 | 3 | 3 | 0 |
| 3 | 441 | 454 | 0 | 454 |
| 4 | 276 | 268 | 268 | 0 |
| 5 | 173 | 163 | 0 | 163 |
| 6 | 82 | 74 | -74 | 0 |
| 7 | 42 | 42 | 0 | -42 |
| 8 | 16 | 14 | 13 | 0 |
| 9 | 71 | 71 | 0 | 71 |
| 10 | 118 | 116 | 116 | 0 |
| 11 | 213 | 216 | 0 | 216 |
| 12 | 68 | 69 | -70 | 0 |
| 13 | 91 | 95 | 0 | 95 |
| 14 | 45 | 45 | -45 | 0 |
| 15 | 14 | 12 | 0 | 12 |
| 16 | 13 | 13 | 13 | 0 |
| | | h40 | | |
| 0 | 40 | 32 | -32 | 0 |
| 1 | 11 | 7 | 0 | 7 |
| 2 | 299 | 297 | 297 | 0 |
| 3 | 128 | 110 | 0 | 110 |
| 4 | 13 | 12 | 12 | 0 |
| 5 | 52 | 45 | 0 | 44 |
| 6 | 74 | 68 | -68 | 0 |
| 7 | 32 | 32 | 0 | 32 |
| 8 | 149 | 153 | 153 | 0 |
| 9 | 45 | 39 | 0 | -39 |
| 10 | 94 | 107 | -107 | 0 |
| 11 | 108 | 119 | 0 | -119 |
| 12 | 163 | 165 | -165 | 0 |
| 13 | 42 | 41 | 0 | -41 |
| 14 | 27 | 23 | 24 | 0 |
| 15 | 18 | 19 | 0 | 19 |
| | | h50 | | |
| 1 | 31 | 31 | 0 | 31 |
| 2 | 249 | 246 | -245 | 0 |
| 3 | 71 | 67 | 0 | -67 |
| 4 | 343 | 336 | -336 | 0 |
| 5 | 34 | 31 | 0 | -31 |
| 6 | 35 | 35 | 35 | 0 |
| 7 | 12 | 2 | 0 | 2 |
| 8 | 34 | 32 | -32 | 0 |
| 9 | 48 | 46 | 0 | -46 |
| 10 | 214 | 213 | -213 | 0 |
| 11 | 42 | 44 | 0 | 44 |
| 12 | 86 | 84 | -84 | 0 |
| 13 | 35 | 33 | 0 | 33 |
| 14 | 33 | 32 | -32 | 0 |
| 15 | 11 | 11 | 0 | -12 |
| | | h60 | | |
| 0 | 146 | 155 | 155 | 0 |
| 1 | 42 | 47 | 0 | -47 |
| 2 | 106 | 109 | 109 | 0 |
| 3 | <15 | 8 | 0 | -8 |
| 4 | <16 | 13 | -13 | 0 |
| 5 | 47 | 49 | 0 | 49 |
| 6 | 38 | 40 | -40 | 0 |
| 7 | 17 | 12 | 0 | -12 |
| 8 | 58 | 64 | 64 | 0 |
| 9 | 48 | 48 | 0 | 48 |
| 10 | 113 | 131 | 131 | 0 |
| 11 | 44 | 46 | 0 | 44 |
| 12 | 66 | 62 | 62 | 0 |
| 13 | 22 | 23 | 0 | -23 |
| 14 | 38 | 37 | -37 | 0 |
| | | h70 | | |
| 1 | 39 | 43 | 0 | 43 |
| 2 | 118 | 129 | 129 | 0 |
| 3 | 39 | 40 | 0 | 40 |
| 4 | 56 | 54 | -55 | 0 |
| 5 | 13 | 13 | 0 | -13 |
| 6 | 9 | 3 | 3 | 0 |
| 7 | 53 | 57 | 0 | 57 |
| 8 | <9 | 1 | 1 | 0 |
| 9 | 74 | 73 | 0 | 73 |
| 10 | 46 | 44 | -44 | 0 |
| 11 | 15 | 17 | 0 | -17 |
| 12 | 16 | 14 | 14 | 0 |
| 13 | 33 | 36 | 0 | -37 |
| | | h80 | | |
| 0 | 180 | 186 | 187 | 0 |
| 1 | 277 | 307 | 0 | 307 |
| 2 | 40 | 41 | -41 | 0 |
| 3 | 42 | 43 | 0 | 43 |
| 4 | 47 | 50 | -50 | 0 |
| 5 | 14 | 15 | 0 | 16 |
| 6 | 58 | 70 | 70 | 0 |
| 7 | 60 | 65 | 0 | 65 |
| 8 | 21 | 21 | -21 | 0 |
| 9 | 55 | 54 | 0 | 54 |
| 10 | <9 | 1 | -1 | 0 |
| 11 | 13 | 11 | 0 | 11 |
| 12 | 14 | 12 | -13 | 0 |
| | | h90 | | |
| 1 | 30 | 21 | 0 | -20 |
| 2 | 105 | 101 | -100 | 0 |
| 3 | 44 | 36 | 0 | 35 |
| 4 | 38 | 33 | 33 | 0 |
| 5 | <24 | 6 | 0 | -3 |
| 6 | <23 | 4 | -4 | 0 |
| 7 | 111 | 92 | 0 | -92 |
| 8 | 60 | 56 | -56 | 0 |
| 9 | 31 | 27 | 0 | -27 |
| 10 | 41 | 31 | -31 | 0 |
| 11 | 24 | 18 | 0 | 18 |
| | | h,10,0 | | |
| 0 | 104 | 90 | -90 | 0 |
| 1 | 36 | 31 | 0 | -30 |
| 2 | 64 | 57 | -57 | 0 |
| 3 | <16 | 8 | 0 | 7 |
| 4 | <15 | 8 | -8 | 0 |
| 5 | <21 | 0 | 0 | -0 |
| 6 | 24 | 21 | -21 | 0 |
| 7 | 37 | 30 | 0 | 30 |
| 8 | 52 | 41 | -41 | 0 |
| 9 | 19 | 17 | 0 | 17 |
| | | h,11,0 | | |
| 1 | 29 | 19 | 0 | 19 |
| 2 | 118 | 93 | -93 | 0 |
| 3 | 59 | 43 | 0 | 43 |
| 4 | 41 | 29 | -29 | 0 |
| 5 | 35 | 25 | 0 | 25 |
| 6 | 40 | 29 | -29 | 0 |
| 7 | 16 | 5 | 0 | -5 |
| | | h,12,0 | | |
| 0 | 11 | 10 | -10 | 0 |
| 1 | 51 | 48 | 0 | 47 |
| 2 | 31 | 25 | 25 | 0 |
| 3 | 26 | 27 | 0 | 27 |
| | | h01 | | |
| 1 | 289 | 296 | 0 | 296 |
| 2 | 560* | 704 | 0 | -704 |
| 3 | 490* | 570 | 0 | 570 |
| 4 | 39 | 31 | 0 | -31 |
| 5 | 44 | 43 | 0 | -43 |
| 6 | 24 | 25 | 0 | -25 |
| 7 | 31 | 22 | 0 | -22 |
| 8 | 108 | 92 | 0 | -92 |
| 9 | 125 | 111 | 0 | 111 |
| 10 | 82 | 72 | 0 | -72 |
| 11 | <14 | 3 | 0 | -4 |
| 12 | 115 | 104 | 0 | -104 |
| 13 | <13 | 8 | 0 | -8 |
| 14 | 30 | 27 | 0 | 27 |
| 15 | 41 | 40 | 0 | -40 |
| 16 | 35 | 35 | 0 | 35 |
| | | h11 | | |
| 0 | 449* | 514 | 0 | -514 |
| 1 | 342* | 391 | -230 | 317 |
| 2 | 228 | 246 | 236 | -64 |
| 3 | 224 | 232 | -219 | 78 |
| 4 | 102 | 92 | 83 | -40 |
| 5 | 159 | 155 | -44 | -148 |
| 6 | 246 | 226 | -107 | -199 |
| 7 | 152 | 138 | -124 | -61 |
| 8 | 53 | 48 | -48 | 7 |
| 9 | 111 | 92 | -68 | -62 |
| 10 | 76 | 67 | 25 | 62 |
| 11 | 36 | 36 | 17 | 32 |
| 12 | 69 | 75 | 36 | 66 |
| 13 | 92 | 89 | 4 | 89 |
| 14 | 35 | 36 | 24 | 26 |
| 15 | 23 | 23 | 20 | 12 |
| 16 | 36 | 43 | -28 | -33 |
| | | h21 | | |
| 0 | 264 | 265 | -265 | 0 |
| 1 | 213 | 209 | -53 | -202 |
| 2 | 162 | 157 | -145 | 59 |
| 3 | 121 | 116 | 115 | -42 |
| 4 | 23 | 15 | 3 | 14 |
| 5 | 100 | 87 | -3 | 87 |
| 6 | 59 | 56 | 44 | -33 |
| 7 | 118 | 107 | -103 | 30 |
| 8 | 71 | 68 | -68 | 3 |
| 9 | 33 | 29 | -6 | -29 |
| 10 | 117 | 118 | -117 | -12 |
| 11 | <14 | 9 | -9 | -3 |
| 12 | 73 | 72 | -13 | -71 |
| 13 | 55 | 52 | 29 | 43 |
| 14 | 56 | 56 | 14 | -55 |
| 15 | 45 | 41 | 18 | 37 |
| 16 | 13 | 15 | 7 | -13 |
| | | h31 | | |
| 0 | 21 | 21 | 0 | -21 |
| 1 | 337 | 335 | -296 | 158 |
| 2 | 189 | 194 | -165 | 103 |
| 3 | 29 | 25 | 4 | 25 |
| 4 | 166 | 146 | -130 | -66 |
| 5 | 81 | 68 | 64 | 24 |
| 6 | 124 | 114 | -70 | -90 |
| 7 | 101 | 98 | 9 | 97 |
| 8 | 81 | 74 | -43 | 60 |
| 9 | 77 | 69 | -67 | -18 |
| 10 | 77 | 77 | -24 | -73 |
| 11 | <14 | 2 | 2 | -2 |
| 12 | 108 | 103 | -73 | -73 |
| 13 | 88 | 82 | 71 | 41 |
| 14 | 89 | 89 | -85 | 26 |
| 15 | 39 | 38 | 24 | -30 |
| | | h41 | | |
| 0 | 97 | 88 | 88 | 0 |
| 1 | 24 | 23 | 10 | -21 |
| 2 | 102 | 91 | 51 | -76 |
| 3 | 98 | 91 | 78 | -47 |
| 4 | 243 | 223 | -81 | -208 |
| 5 | 234 | 220 | 78 | 204 |
| 6 | 71 | 67 | -64 | 20 |
| 7 | 79 | 77 | 73 | -25 |
| 8 | 128 | 123 | 79 | -94 |
| 9 | 184 | 198 | 118 | -160 |
| 10 | 200 | 204 | 81 | -187 |
| 11 | 64 | 62 | 62 | -4 |
| 12 | 17 | 17 | 17 | 4 |
| 13 | 11 | 11 | -6 | -9 |
| 14 | 13 | 14 | 2 | 13 |
| 15 | 23 | 25 | 9 | -23 |
| | | h51 | | |
| 0 | 188 | 189 | 0 | -189 |
| 1 | 151 | 151 | -31 | -148 |
| 2 | 174 | 170 | 83 | -148 |
| 3 | 114 | 110 | 18 | -109 |
| 4 | 92 | 84 | 46 | 70 |
| 5 | 99 | 87 | -58 | -65 |
| 6 | 69 | 62 | 13 | 61 |
| 7 | 95 | 94 | -6 | - 93 |
| 8 | 93 | 95 | -24 | -92 |
| 9 | 39 | 38 | -38 | -2 |
| 10 | 24 | 22 | 12 | 19 |
| 11 | 81 | 73 | -56 | -46 |
| 12 | 89 | 82 | 40 | 71 |
| 13 | 107 | 106 | 17 | -105 |
| 14 | 26 | 24 | -18 | 16 |
| | | h61 | | |
| 0 | 71 | 77 | 77 | 0 |
| 1 | 98 | 95 | 20 | 93 |
| 2 | 55 | 50 | 49 | -8 |
| 3 | 38 | 38 | -35 | 18 |
| 4 | 38 | 31 | 8 | -30 |
| 5 | 28 | 23 | 14 | -19 |
| 6 | 47 | 46 | -34 | 30 |
| 7 | 42 | 39 | 28 | 26 |
| 8 | 69 | 72 | -1 | 72 |
| 9 | 64 | 64 | -12 | 63 |
| 10 | 35 | 35 | 26 | 23 |
| 11 | 70 | 71 | 55 | 45 |
| 12 | 51 | 50 | -33 | -37 |
| 13 | 43 | 45 | 42 | 17 |
| 14 | 33 | 37 | -23 | -29 |
| | | h71 | | |
| 0 | 42 | 43 | 0 | 43 |
| 1 | 114 | 110 | -110 | -9 |
| 2 | 113 | 122 | 88 | -84 |
| 3 | 91 | 89 | -38 | 81 |
| 4 | 73 | 79 | -6 | -78 |
| 5 | 43 | 43 | -18 | 39 |
| 6 | 66 | 67 | -67 | -4 |
| 7 | 84 | 85 | -58 | -63 |
| 8 | 61 | 60 | -29 | -53 |
| 9 | 9 | 7 | 3 | 6 |
| 10 | 15 | 16 | 2 | -16 |
| 11 | 60 | 61 | 46 | 40 |
| 12 | 47 | 43 | 43 | -5 |
| 13 | 27 | 27 | 26 | 8 |
| | | h81 | | |
| 0 | 92 | 97 | -97 | 0 |
| 1 | 102 | 103 | 95 | -41 |
| 2 | 156 | 162 | -126 | -103 |
| 3 | 146 | 138 | 107 | 87 |
| 4 | 67 | 77 | -67 | 37 |
| 5 | 22 | 17 | 16 | - 2 |
| 6 | 10 | 10 | 10 | -1 |
| 7 | 24 | 24 | 21 | -12 |
| 8 | 34 | 34 | -21 | -26 |
| 9 | 48 | 44 | 43 | 8 |
| 10 | 25 | 25 | -24 | -7 |
| 11 | 64 | 62 | 52 | -34 |
| 12 | 24 | 27 | 2 | -27 |
| | | h91 | | |
| 0 | 141 | 136 | 0 | -136 |
| 1 | 90 | 87 | 56 | 66 |
| 2 | 48 | 52 | -34 | -39 |
| 3 | 32 | 30 | 14 | 27 |
| 4 | <16 | 14 | 13 | -5 |
| 5 | 77 | 81 | 68 | -44 |
| 6 | 59 | 62 | 20 | -59 |
| 7 | 23 | 24 | 22 | -9 |
| 8 | 41 | 43 | 26 | -34 |
| 9 | 31 | 31 | -28 | -13 |
| 10 | 10 | 9 | 4 | -8 |
| | | h,10,1 | | |
| 0 | 63 | 61 | 61 | 0 |
| 1 | 66 | 64 | -25 | -60 |
| 2 | 39 | 36 | 32 | 17 |
| 3 | 35 | 28 | -2 | -29 |
| 4 | 26 | 22 | -21 | 7 |
| 5 | <14 | 7 | 4 | 5 |
| 6 | 25 | 23 | -13 | -19 |
| 7 | <13 | 12 | -9 | -8 |
| | | h,11,1 | | |
| 0 | 69 | 69 | 0 | -69 |
| 1 | 30 | 28 | -27 | 6 |
| 2 | 19 | 15 | -12 | -9 |
| 3 | 34 | 35 | 10 | -33 |
| 4 | 11 | 10 | -5 | 9 |
| 5 | 43 | 43 | 23 | -37 |
| 6 | 29 | 30 | -30 | -3 |
| | | h02 | | |
| 0 | 48 | 49 | 49 | 0 |
| 1 | 173 | 174 | -174 | 0 |
| 2 | 36 | 32 | 32 | 0 |
| 3 | 136 | 119 | 119 | 0 |
| 4 | 19 | 18 | 18 | 0 |
| 5 | 296 | 252 | 252 | 0 |
| 6 | 68 | 48 | 48 | 0 |
| 7 | 23 | 24 | -24 | 0 |
| 8 | 16 | 19 | 19 | 0 |
| 9 | 22 | 22 | 22 | 0 |
| 10 | 31 | 30 | -30 | 0 |
| 11 | 14 | 13 | 13 | 0 |
| 12 | 66 | 69 | -69 | 0 |
| 13 | <11 | 6 | -6 | 0 |
| 14 | 16 | 16 | 16 | 0 |
| 15 | 34 | 35 | 35 | 0 |
| | | h12 | | |
| 0 | 13 | 2 | 0 | -2 |
| 1 | 27 | 23 | 11 | -20 |
| 2 | 160 | 153 | -147 | -43 |
| 3 | 346 | 328 | 315 | 91 |
| 4 | 235 | 223 | -64 | -214 |
| 5 | 148 | 136 | 109 | 82 |
| 6 | 141 | 134 | 37 | -128 |
| 7 | 17 | 17 | 11 | -13 |
| 8 | 21 | 20 | 0 | 20 |
| 9 | 50 | 51 | -17 | 49 |
| 10 | 73 | 76 | -76 | 8 |
| 11 | 108 | 103 | -81 | 64 |
| 12 | 40 | 38 | -37 | -10 |
| 13 | 38 | 39 | -5 | 38 |
| 14 | 34 | 29 | 14 | -26 |
| 15 | 24 | 25 | -3 | 25 |
| | | h22 | | |
| 0 | 64 | 66 | 66 | 0 |
| 1 | 119 | 129 | -65 | -111 |
| 2 | 110 | 111 | 83 | 74 |
| 3 | 135 | 130 | -107 | 73 |
| 4 | 92 | 84 | 84 | -12 |
| 5 | 43 | 38 | -36 | -11 |
| 6 | 45 | 41 | 20 | -34 |
| 7 | 44 | 40 | 39 | -4 |
| 8 | 96 | 100 | -3 | -99 |
| 9 | 34 | 36 | 34 | -11 |
| 10 | 51 | 56 | 47 | -30 |
| 11 | 42 | 41 | -12 | -40 |
| 12 | 40 | 42 | 33 | 26 |
| 13 | 12 | 11 | -1 | 11 |
| 14 | 33 | 33 | -29 | -14 |
| 15 | 47 | 54 | 51 | 17 |
| | | h32 | | |
| 0 | 55 | 49 | 0 | -49 |
| 1 | 93 | 93 | -88 | 32 |
| 2 | 79 | 73 | 36 | -64 |
| 3 | 60 | 62 | 55 | -29 |
| 4 | 19 | 18 | -18 | 2 |
| 5 | 49 | 51 | -49 | -15 |
| 6 | 70 | 68 | -59 | 34 |
| 7 | 81 | 84 | 49 | 68 |
| 8 | 51 | 53 | 10 | 52 |
| 9 | 72 | 77 | 74 | 23 |
| 10 | 28 | 26 | 8 | 25 |
| 11 | 30 | 26 | -25 | -8 |
| 12 | 50 | 48 | -41 | -24 |
| 13 | 49 | 46 | 44 | -11 |
| 14 | 36 | 36 | -21 | 29 |
| | | h42 | | |
| 0 | 211 | 206 | 206 | 0 |
| 1 | 137 | 138 | 44 | 131 |
| 2 | 90 | 87 | 81 | -33 |
| 3 | 82 | 76 | -70 | 29 |
| 4 | 35 | 34 | -33 | 10 |
| 5 | 79 | 74 | 73 | -3 |
| 6 | 143 | 142 | 35 | 137 |
| 7 | 244 | 259 | 256 | 39 |
| 8 | 137 | 140 | 74 | 119 |
| 9 | 52 | 50 | 30 | 40 |
| 10 | 26 | 23 | -3 | 23 |
| 11 | 12 | 11 | -10 | 4 |
| 12 | 21 | 18 | -9 | 16 |
| 13 | 67 | 61 | 59 | -15 |
| 14 | 25 | 24 | -16 | 18 |
| | | h52 | | |
| 0 | 94 | 96 | 0 | 96 |
| 1 | 87 | 86 | 80 | 32 |
| 2 | 38 | 35 | -35 | -4 |
| 3 | 27 | 23 | -20 | 11 |
| 4 | 49 | 46 | 25 | -38 |
| 5 | 29 | 29 | 26 | 11 |
| 6 | 43 | 43 | 9 | -42 |
| 7 | 75 | 72 | -66 | 28 |
| 8 | 70 | 67 | -60 | -29 |
| 9 | 66 | 65 | -65 | -9 |
| 10 | 32 | 28 | -20 | 20 |
| 11 | 47 | 47 | 41 | 23 |
| 12 | 44 | 40 | 27 | -30 |
| 13 | 49 | 47 | -29 | 32 |
| | | h62 | | |
| 0 | 86 | 88 | -88 | 0 |
| 1 | 61 | 60 | 17 | 57 |
| 2 | 46 | 45 | -11 | -44 |
| 3 | 16 | 15 | 4 | 14 |
| 4 | 48 | 48 | 43 | -20 |
| 5 | 68 | 69 | -40 | 54 |
| 6 | 17 | 12 | -6 | -11 |
| 7 | 57 | 54 | -53 | 8 |
| 8 | 54 | 49 | -26 | 42 |
| 9 | 42 | 38 | -38 | 2 |
| 10 | 16 | 16 | -14 | 8 |
| 11 | 47 | 42 | -20 | 36 |
| 12 | 10 | 11 | 5 | -10 |
| | | h72 | | |
| 0 | <9 | 0 | 0 | 0 |
| 1 | 24 | 24 | 15 | 17 |
| 2 | 65 | 68 | -8 | -67 |
| 3 | 62 | 62 | -8 | 62 |
| 4 | 122 | 140 | -43 | -133 |
| 5 | 106 | 106 | 105 | 18 |
| 6 | 57 | 54 | -26 | -47 |
| 7 | 50 | 48 | 42 | -24 |
| 8 | 30 | 29 | -14 | 25 |
| 9 | 48 | 46 | -28 | 37 |
| 10 | 40 | 37 | -18 | 32 |
| 11 | 51 | 47 | 22 | 42 |
| | | h82 | | |
| 0 | 36 | 34 | 34 | 0 |
| 1 | 83 | 80 | -79 | 12 |
| 2 | 12 | 8 | 7 | -3 |
| 3 | 10 | 12 | -9 | 8 |
| 4 | 76 | 79 | -19 | 77 |
| 5 | 64 | 66 | 65 | 12 |
| 6 | 51 | 52 | -5 | 52 |
| 7 | 19 | 16 | -3 | 16 |
| 8 | 23 | 18 | 18 | 3 |
| 9 | 28 | 27 | 26 | -4 |
| 10 | 13 | 12 | 11 | 4 |
| | | h92 | | |
| 0 | 23 | 20 | 0 | 21 |
| 1 | 41 | 38 | -5 | -38 |
| 2 | 79 | 78 | -31 | 71 |
| 3 | 110 | 109 | 104 | -32 |
| 4 | 61 | 67 | -31 | 60 |
| 5 | 50 | 51 | 51 | 4 |
| 6 | 17 | 19 | -4 | 19 |
| 7 | 10 | 10 | 8 | -5 |
| 8 | 17 | 18 | -13 | 13 |
| 9 | 14 | 15 | 0 | -15 |
| | | h,10,2 | | |
| 0 | 24 | 23 | 23 | 0 |
| 1 | 19 | 21 | -13 | 16 |
| 2 | 37 | 33 | 8 | -32 |
| 3 | 58 | 52 | -19 | 48 |
| 4 | 34 | 36 | 5 | -34 |
| 5 | <8 | 4 | 1 | 4 |
| 6 | 16 | 15 | 2 | 14 |
| | | h,11,2 | | |
| 0 | 8 | 8 | 0 | -8 |
| 1 | 24 | 24 | -6 | 23 |
| 2 | 12 | 14 | 11 | -8 |
| | | h03 | | |
| 1 | 16 | 17 | 0 | 17 |
| 2 | 99 | 99 | 0 | 99 |
| 3 | 197 | 180 | 0 | 180 |
| 4 | 13 | 14 | 0 | -14 |
| 5 | 78 | 70 | 0 | 70 |
| 6 | 32 | 29 | 0 | -29 |
| 7 | 15 | 15 | 0 | -15 |
| 8 | 48 | 46 | 0 | -46 |
| 9 | 43 | 42 | 0 | -42 |
| 10 | 85 | 79 | 0 | -78 |
| 11 | 27 | 27 | 0 | -27 |
| 12 | 21 | 18 | 0 | 18 |
| 13 | 21 | 23 | 0 | 23 |
| | | h13 | | |
| 0 | 32 | 30 | 0 | 30 |
| 1 | 43 | 43 | 5 | 43 |
| 2 | 26 | 26 | -5 | 25 |
| 3 | 38 | 36 | -25 | -25 |
| 4 | 113 | 103 | 25 | 100 |
| 5 | 105 | 94 | 27 | -91 |
| 6 | 115 | 115 | -66 | 93 |
| 7 | 51 | 52 | 35 | -39 |
| 8 | 68 | 65 | -50 | -41 |
| 9 | 32 | 30 | -7 | -29 |
| 10 | 29 | 29 | -1 | -29 |
| 11 | 8 | 7 | -0 | -6 |
| 12 | 32 | 31 | -23 | 21 |
| 13 | 16 | 18 | 6 | -17 |
| | | h23 | | |
| 0 | 38 | 36 | -35 | 0 |
| 1 | 58 | 55 | -55 | 1 |
| 2 | 36 | 36 | 35 | 8 |
| 3 | 38 | 38 | -37 | 9 |
| 4 | 37 | 36 | -8 | -35 |
| 5 | 71 | 70 | 64 | 30 |
| 6 | 63 | 71 | -38 | -60 |
| 7 | 66 | 71 | 53 | 47 |
| 8 | 26 | 28 | 26 | -9 |
| 9 | 57 | 60 | 56 | 21 |
| 10 | 24 | 30 | -13 | 19 |
| 11 | 27 | 25 | 25 | -0 |
| 12 | 23 | 23 | -16 | -14 |
| 13 | 22 | 26 | -9 | 24 |
| | | h33 | | |
| 0 | 30 | 31 | 0 | 31 |
| 1 | 25 | 24 | -11 | 22 |
| 2 | 66 | 70 | 52 | -47 |
| 3 | 45 | 47 | -47 | -3 |
| 4 | 67 | 69 | -46 | -52 |
| 5 | 114 | 120 | -118 | 25 |
| 6 | 72 | 75 | -67 | 34 |
| 7 | 67 | 74 | -60 | 44 |
| 8 | 53 | 49 | -46 | 15 |
| 9 | 45 | 44 | 27 | 35 |
| 10 | 14 | 8 | -8 | -1 |
| 11 | <10 | 3 | -2 | -2 |
| 12 | 18 | 18 | 9 | 13 |
| | | h43 | | |
| 0 | 36 | 38 | -38 | 0 |
| 1 | 46 | 47 | 28 | 37 |
| 2 | 82 | 83 | -47 | -68 |
| 3 | 68 | 68 | 20 | 65 |
| 4 | 75 | 78 | -58 | 51 |
| 5 | 105 | 107 | -27 | 104 |
| 6 | 52 | 46 | -23 | 40 |
| 7 | 47 | 46 | -37 | -28 |
| 8 | 19 | 20 | 19 | 4 |
| 9 | 56 | 56 | -30 | -47 |
| 10 | 45 | 43 | 8 | 43 |
| 11 | 25 | 20 | -7 | 19 |
| 12 | <6 | 5 | 4 | -3 |
| | | h53 | | |
| 0 | 48 | 47 | 0 | -47 |
| 1 | 21 | 21 | -17 | 12 |
| 2 | 41 | 40 | 40 | -3 |
| 3 | 23 | 22 | -18 | 13 |
| 4 | 45 | 45 | -7 | -44 |
| 5 | 64 | 69 | -15 | -67 |
| 6 | 106 | 102 | 12 | -102 |
| 7 | 86 | 80 | 12 | -80 |
| 8 | 19 | 17 | -11 | -13 |
| 9 | 26 | 22 | 22 | 5 |
| 10 | 23 | 22 | -16 | 14 |
| 11 | 6 | 7 | -3 | -7 |
| | | h63 | | |
| 0 | 28 | 30 | 30 | 0 |
| 1 | 16 | 16 | 12 | -11 |
| 2 | 54 | 59 | -22 | 55 |
| 3 | 20 | 19 | 9 | -17 |
| 4 | 21 | 20 | -16 | -12 |
| 5 | 25 | 24 | 13 | 20 |
| 6 | 80 | 72 | -8 | -72 |
| 7 | 45 | 41 | 36 | 19 |
| 8 | 73 | 69 | -38 | -58 |
| 9 | 10 | 10 | -7 | -8 |
| 10 | 17 | 19 | 1 | -19 |
| | | h73 | | |
| 0 | 22 | 20 | 0 | -20 |
| 1 | 37 | 39 | 29 | -24 |
| 2 | 9 | 6 | 6 | -2 |
| 3 | 25 | 25 | 24 | 5 |
| 4 | 14 | 13 | -13 | - 1 |
| 5 | 59 | 57 | 56 | 11 |
| 6 | 68 | 64 | -64 | 3 |
| 7 | 38 | 39 | 20 | -34 |
| 8 | 47 | 45 | -34 | 30 |
| 9 | 22 | 24 | -22 | -9 |
| | | h83 | | |
| 0 | <9 | 9 | -9 | 0 |
| 1 | 30 | 31 | -25 | -16 |
| 2 | 53 | 52 | -49 | 13 |
| 3 | 52 | 52 | -22 | 48 |
| 4 | 64 | 69 | -66 | -19 |
| 5 | 17 | 13 | 11 | 7 |
| 6 | 19 | 20 | -14 | 14 |
| 7 | 22 | 26 | 26 | -6 |
| | | h93 | | |
| 0 | 19 | 18 | 0 | 18 |
| 1 | 20 | 23 | -6 | 22 |
| 2 | <8 | 7 | 1 | -7 |
| 3 | 42 | 48 | -47 | 3 |
| 4 | 35 | 45 | 44 | 3 |
| | | h04 | | |
| 0 | 117 | 101 | -101 | 0 |
| 1 | 27 | 28 | -28 | 0 |
| 2 | 32 | 28 | -28 | 0 |
| 3 | 22 | 19 | -19 | 0 |
| 4 | <13 | 1 | 1 | 0 |
| 5 | 67 | 55 | 55 | 0 |
| 6 | 13 | 14 | -14 | 0 |
| 7 | 106 | 97 | 97 | 0 |
| 8 | 18 | 16 | 16 | 0 |
| 9 | 43 | 43 | 43 | 0 |
| | | h14 | | |
| 0 | 42 | 45 | 0 | -43 |
| 1 | 13 | 12 | -8 | -9 |
| 2 | 13 | 13 | 13 | 1 |
| 3 | 15 | 14 | -4 | -13 |
| 4 | <9 | 4 | -3 | 2 |
| 5 | 26 | 27 | -17 | 21 |
| 6 | 48 | 46 | 40 | -23 |
| 7 | 45 | 42 | -32 | 28 |
| 8 | 31 | 32 | 29 | 15 |
| 9 | 21 | 23 | -23 | -4 |
| | | h24 | | |
| 0 | <18 | 1 | 1 | 0 |
| 1 | 23 | 22 | 17 | -14 |
| 2 | 36 | 33 | 29 | 16 |
| 3 | 21 | 20 | 20 | 1 |
| 4 | 64 | 59 | 50 | -32 |
| 5 | 18 | 18 | -12 | 13 |
| 6 | 43 | 41 | 8 | 40 |
| 7 | 14 | 14 | -10 | - 10 |
| 8 | 60 | 63 | -32 | 54 |
| 9 | 26 | 30 | 24 | -18 |
| | | h34 | | |
| 0 | <19 | 9 | 0 | 9 |
| 1 | 37 | 32 | 21 | -24 |
| 2 | 63 | 64 | 20 | -61 |
| 3 | 46 | 41 | -19 | -36 |
| 4 | 106 | 98 | -41 | -89 |
| 5 | 14 | 16 | -12 | -11 |
| 6 | 48 | 47 | -33 | -34 |
| 7 | 34 | 33 | 31 | 10 |
| 8 | 23 | 22 | -11 | -18 |
| | | h44 | | |
| 0 | <16 | 7 | 7 | 0 |
| 1 | 24 | 21 | -20 | -5 |
| 2 | 32 | 28 | -28 | 4 |
| 3 | <15 | 7 | -6 | -4 |
| 4 | 18 | 18 | -2 | 18 |
| 5 | 49 | 44 | 43 | 7 |
| 6 | 33 | 31 | 29 | 9 |
| 7 | 10 | 9 | 9 | 3 |
| | | h54 | | |
| 0 | <13 | 4 | 0 | 4 |
| 1 | 19 | 18 | 10 | -16 |
| 2 | 19 | 18 | 10 | -15 |
| 3 | 79 | 83 | 83 | -1 |
| 4 | 45 | 41 | 41 | -3 |
| 5 | 66 | 71 | 64 | 29 |
| 6 | 11 | 10 | 8 | 6 |
| | | h64 | | |
| 0 | 21 | 22 | -22 | 0 |
| 1 | 16 | 16 | 9 | 13 |
| 2 | 8 | 8 | 0 | -8 |
| 3 | 30 | 32 | -5 | 32 |
| 4 | 33 | 35 | 26 | 24 |
| 5 | 13 | 18 | -4 | 17 |
| | | h74 | | |
| 0 | 5 | 6 | 0 | -6 |
| 1 | 18 | 22 | 21 | -8 |

amino nitrogen atom N(8) to O(7) atoms and one from N(1) to N(3). The two N · · · O distances, 2·98 and 3·03 Å, are a bit longer than are often found in purines and pyrimidines; the N · · · N distance, 2·84 Å, is a bit shorter (see, for example, Fuller, 1959).

Two features of the hydrogen-bond network are noteworthy: the arrangement of N–H · · · O bonds to form spirals up the twofold screw axes parallel to *c*, and the arrangement of N–H · · · O and N–H · · · N bonds to form ribbons of molecules along *b*. The ribbons of molecules along *b* are very similar to those occurring in cytosine monohydrate (Jeffrey & Kinoshita, 1963). The N · · · N hydrogen-bond distance within the ribbons is longer in cytosine monohydrate (2·95 Å) and adjacent molecules are more nearly parallel (the dihedral angle is about 2° in cytosine monohydrate and about 15° in cytosine); as a consequence, the length of the *b* axis is slightly longer (9·84 *versus* 9·50 Å).

The molecules are tilted about 27½° from parallel to the *ab* plane, and the interplanar distance between successive molecules along *c* is 3·36 Å. Other close

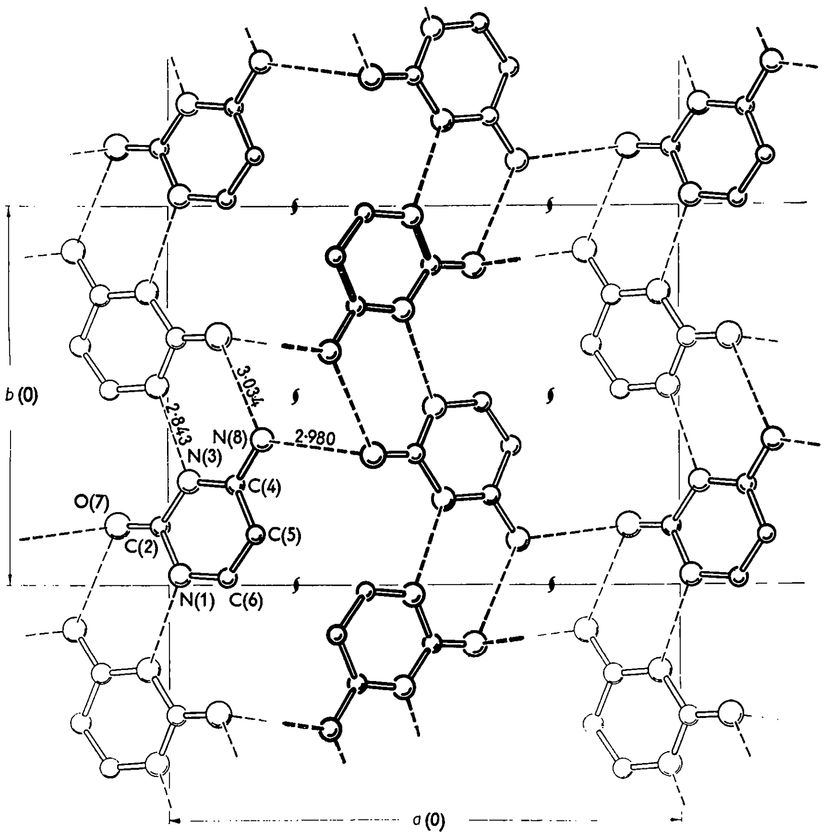

Fig. 4. The structure viewed down the $c$ axis. The dashed lines represent hydrogen bonds.

intermolecular contacts are N(8)–N(8), 3·40 Å, and C(5)–C(6), 3·58 Å, both contacts being between molecules related by a screw axis parallel to $c$.

### *The temperature factors*

The magnitudes and direction cosines of the principal axes of thermal motion of the heavy atoms, derived from the anisotropic temperature parameters of Table 2, are listed in Table 4. The temperature motions are shown in Fig. 5, in which the three equatorial ellipses (that is, the ellipses defined by pairs of principal axes) are viewed both parallel and perpendicular to the molecular plane. A corresponding representation of the temperature motions in cytosine monohydrate, based on the parameters of Jeffrey & Kinoshita (1963), is also shown in Fig. 5.

Although there are pronounced differences in the lattice vibrations in the two structures — cytosine has a relatively large translational amplitude parallel to $c$ and cytosine monohydrate a relatively small amplitude along $b$ — the general pattern of molecular motion is strikingly similar in the two structures, leaving little doubt as to its reality. The largest amplitudes are out-of-plane, and the relative values suggest not only rigid-body motions about in-plane axes but, in addition, either a buckling of the molecule

Table 4. *The magnitudes B and direction cosines q, relative to the crystallographic axes, of the principal axes of the temperature factor ellipsoids*

| Atom | Axis $i$ | $B_i$ | $q_i^a$ | $q_i^b$ | $q_i^c$ |
|---|---|---|---|---|---|
| N(1) | 1 | 3·03 | 0·033 | −0·024 | 0·999 |
| | 2 | 2·17 | 0·966 | −0·257 | −0·038 |
| | 3 | 1·80 | 0·258 | 0·966 | 0·015 |
| C(2) | 1 | 2·59 | 0·413 | −0·115 | 0·903 |
| | 2 | 2·00 | 0·488 | 0·866 | −0·113 |
| | 3 | 1·85 | 0·769 | −0·487 | −0·413 |
| N(3) | 1 | 2·94 | 0·061 | 0·010 | 0·998 |
| | 2 | 1·94 | 0·890 | 0·453 | −0·059 |
| | 3 | 1·55 | −0·453 | 0·891 | 0·019 |
| C(4) | 1 | 2·57 | 0·111 | −0·015 | 0·994 |
| | 2 | 2·39 | −0·008 | 1·000 | 0·016 |
| | 3 | 1·89 | 0·994 | 0·009 | −0·111 |
| C(5) | 1 | 3·26 | −0·271 | 0·177 | 0·946 |
| | 2 | 2·94 | 0·423 | 0·905 | −0·048 |
| | 3 | 1·75 | 0·865 | −0·387 | 0·320 |
| C(6) | 1 | 3·06 | 0·741 | 0·419 | 0·524 |
| | 2 | 2·66 | 0·421 | 0·318 | −0·850 |
| | 3 | 1·85 | −0·523 | 0·850 | 0·059 |
| O(7) | 1 | 4·10 | −0·245 | 0·008 | 0·970 |
| | 2 | 2·50 | −0·060 | 0·998 | −0·024 |
| | 3 | 1·68 | 0·968 | 0·064 | 0·244 |
| N(8) | 1 | 4·61 | 0·326 | −0·051 | −0·944 |
| | 2 | 2·62 | 0·586 | −0·772 | 0·245 |
| | 3 | 1·76 | 0·742 | 0·633 | 0·222 |

along its central C(2) · · · C(4) axis or a simple bending of the C(2)–O(7) and C(4)–N(8) bonds. The in-plane motion, on the other hand, can be adequately described as a rigid-body libration with the center of oscillation near C(2) and N(3). The r.m.s. amplitude of this libration appears to be about 2°.

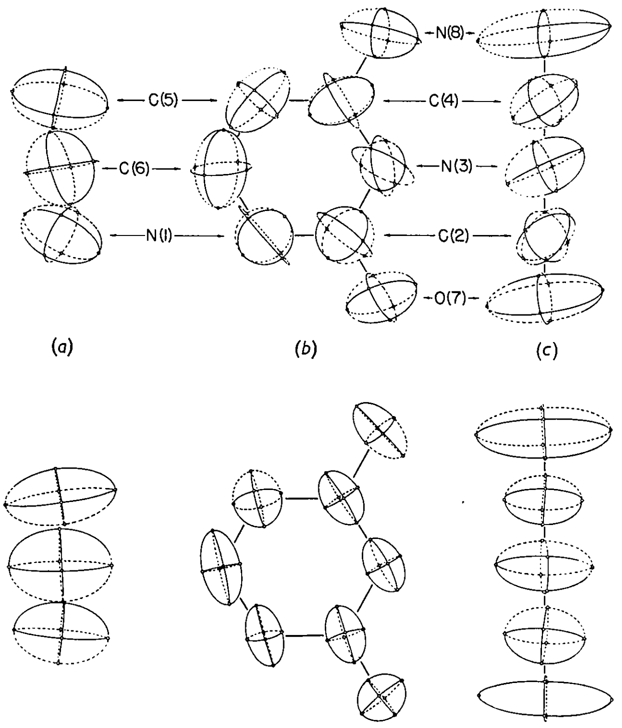

Fig. 5. The ellipses defined by the principal axes of thermal motion, viewed perpendicular (*b*) and parallel (*a* and *c*) to the molecular planes. Top: cytosine, this investigation. Bottom: cytosine monohydrate, Jeffrey & Kinoshita (1963).

The effects of the rigid-body motions on the bond distances and angles are very small — less than 0·002 Å in the distances — and were ignored. The large out-of-plane amplitudes of O(7) and N(8), which suggest non-rigid-body motions, are more important and we estimate that the C(2)–O(7) and C(4)–N(8) distances should be increased by about 0·01 Å for both anhydrous cytosine and cytosine monohydrate.

### *Geometry of the molecule*

The cytosine molecule is very slightly but significantly non-planar. Deviations of the six ring atoms from their best plane are of doubtful significance (Plane *A*, Table 5), the maximum deviations of 0·007 Å being only three times the standard deviations in the atomic positions. The non-ring atoms O(7) and N(8), however, are both displaced slightly to one side of the ring plane. In cytosine monohydrate the deviations from planarity are greater, the ring being buckled and the non-ring atoms lying on opposite sides of — and considerably further from — the best plane of the ring.

Table 5. *Deviations from the least-squares planes*

Plane *A*, ring atoms (1–6):

$0{\cdot}4568X - 0{\cdot}1257Y - 0{\cdot}8806Z = -1{\cdot}3839$ Å

Plane *B*, all heavy atoms (1–8):

$0{\cdot}4595X - 0{\cdot}1298Y - 0{\cdot}8787Z = -1{\cdot}3793$ Å

| Atom | Deviation from plane *A* | Deviation from plane *B* |
|---|---|---|
| N(1) | 0·004 Å | 0·002 Å |
| C(2) | 0·001 | −0·007 |
| N(3) | −0·007 | −0·018 |
| C(4) | 0·007 | 0·001 |
| C(5) | −0·001 | 0·000 |
| C(6) | −0·004 | −0·001 |
| O(7) | 0·025 | 0·013 |
| N(8) | 0·018 | 0·010 |
| H(9) | 0·07 | 0·07 |
| H(10) | −0·10 | −0·09 |
| H(11) | −0·12 | −0·11 |
| H(12) | −0·06 | −0·07 |
| H(13) | 0·15 | 0·14 |

The bond distances and angles calculated from the parameters of Table 2 are shown in Fig. 6 and listed in Table 6; the values found in cytosine monohydrate and in cytosine-5-acetic acid (Marsh *et al.*, 1962) are also listed in Table 6. Differences in bond distances between the two forms of cytosine are of doubtful significance with the exception of the C(2)–O(7) bond,

Table 6. *Comparison of bond distances and angles in anhydrous cytosine, cytosine monohydrate, and cytosine-5-acetic acid*

| Bond distance | Anhydrous cytosine ($\sigma = 0{\cdot}003$ Å) | Cytosine monohydrate ($\sigma = 0{\cdot}004$ Å) | Cytosine-5-acetic acid ($\sigma = 0{\cdot}006$ Å) |
|---|---|---|---|
| N(1)–C(2) | 1·374 Å | 1·376 Å | 1·351 Å |
| C(2)–N(3) | 1·364 | 1·354 | 1·366 |
| N(3)–C(4) | 1·337 | 1·351 | 1·353 |
| C(4)–C(5) | 1·424 | 1·432 | 1·427 |
| C(5)–C(6) | 1·342 | 1·348 | 1·363 |
| C(6)–N(1) | 1·357 | 1·361 | 1·365 |
| C(2)–O(7) | 1·234 | 1·260 | 1·250 |
| C(4)–N(8) | 1·330 | 1·332 | 1·323 |
| Bond angle | ($\sigma = 0{\cdot}2°$) | ($\sigma = 0{\cdot}2°$) | ($\sigma = 0{\cdot}3°$) |
| N(1)–C(2)–N(3) | 118·1° | 120·1° | 117·6° |
| C(2)–N(3)–C(4) | 119·9 | 118·9 | 121·9 |
| N(3)–C(4)–C(5) | 122·0 | 122·0 | 120·7 |
| C(4)–C(5)–C(6) | 117·3 | 117·1 | 115·6 |
| C(5)–C(6)–N(1) | 120·1 | 120·6 | 122·1 |
| C(6)–N(1)–C(2) | 122·7 | 121·3 | 122·0 |
| N(1)–C(2)–O(7) | 119·8 | 118·4 | 121·3 |
| N(3)–C(2)–O(7) | 122·2 | 121·5 | 121·1 |
| N(3)–C(4)–N(8) | 118·2 | 117·8 | 117·3 |
| C(5)–C(4)–N(8) | 119·9 | 120·2 | 121·9 |

which is clearly longer in the monohydrate. This lengthening can undoubtedly be attributed to the increased hydrogen bonding in cytosine monohydrate, where O(7) accepts three hydrogen bonds compared with two in anhydrous cytosine. Differences in many of the bond angles are of significance, and are perhaps the result of different intermolecular environments.

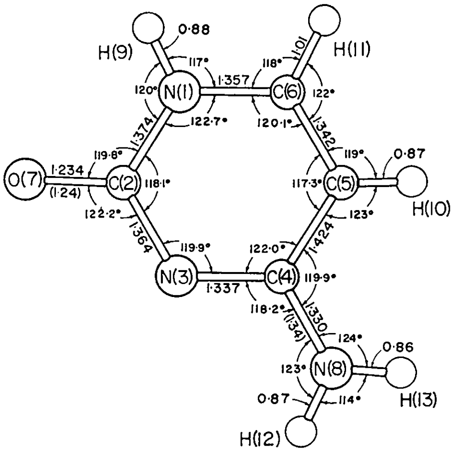

Fig. 6. Bond distances and angles.

Comparisons with cytosine-5-acetic acid are probably not warranted, for in the crystal structure of that compound the ring nitrogen atom N(1) is protonated one-half the time and the charge distribution in the molecule is no doubt altered.

Seven canonical structures for cytosine are shown in Fig. 7. The observed bond distances can be explained reasonably well by assuming the percentage contributions to the resonance hybrid as indicated in the figure, the calculated distances shown in the final drawing being derived from the empirical bond-number–bond-distance curves discussed by Marsh *et al.* (1962).

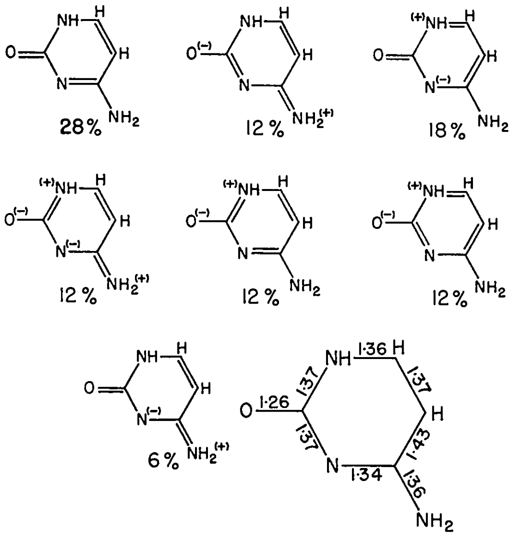

Fig. 7. Canonical structures for the cytosine molecule and the predicted bond distances.

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