THE DETERMINATION OF THE CRYSTAL STRUCTURE OF

THREE ORGANIC COMPOUNDS BY

X-RAY DIFFRACTION

BY

ROGER MICHAEL SCHAFFRIN

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Department of ___Chemistry___

The University of British Columbia
Vancouver 8, Canada

Date ___October 6, 1970___

ABSTRACT

Supervisor: Professor James Trotter

The crystal structure of dibenzothiophene has been determined by X-ray diffraction. Mo-K$_\alpha$ scintillation counter data were used for this analysis; the sulfur atom position was determined by means of a Patterson function; the carbon atoms were located from a Fourier synthesis, and the hydrogen atoms, from a difference synthesis. Refinement of positional and thermal parameters was by least-squares methods. The molecule is slightly folded, the dihedral angles between the five-membered ring and the six-membered rings being 0.4° and 1.2°. The bond distances and valency angles are similar to those in related molecules. The C-S bond length is 1.740 $\overset{o}{A}$, and the C-S-C angle is 91.5°.

The crystal structure of DL-ornithine hydrobromide has been determined by means of visual Cu-K$_\alpha$ data. The bromine ion position was found by Patterson methods; carbon, nitrogen, and oxygen atoms were located on Fourier summations and the hydrogen atoms, on a difference synthesis. The positional and thermal parameters were refined by least-squares. The ornithine molecule is a zwitterion, with both nitrogens accepting protons. The mean bond distances are C-O, 1.249 $\overset{o}{A}$; C-N, 1.469 $\overset{o}{A}$; C-C, 1.532 $\overset{o}{A}$. The structure is held together by a system of N—H....O (2.84, 2.84, 2.89 $\overset{o}{A}$) and N—H...Br (3.29, 3.36, 3.46 $\overset{o}{A}$) hydrogen bonds.

The crystal and molecular structure of histamine diphosphate monohydrate has been determined with scintillation counter Mo-K$_\alpha$ data.

The positions of the phosphorus atoms were determined by Patterson methods; the carbon, nitrogen and oxygen atoms were located by means of Fourier syntheses; the hydrogen atoms were found on a difference synthesis. The thermal and positional parameters were refined by least-squares. The atoms of this histamine cation lie in two almost perpendicular planes, the plane of the imidazole ring and that of the side chain. The bond lengths and angles are similar to the corresponding values in histidine hydrochloride monohydrate. The dimensions of the two $PO_2(OH)_2^-$ ions are P-O 1.51 Å, P-OH 1.57 Å, O-P-O 115.5°, and HO-P-OH 107.0°. The most important feature of the packing is a complex system of O-H...O and N-H...O hydrogen bonds.

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GENERAL INTRODUCTION

In 1912 von Laue suggested that crystals should diffract X-rays; this was confirmed experimentally by Friedrich and Knipping. Bragg elucidated the mathematical interpretation of X-ray diffraction and determined the first crystal structure by X-ray diffraction in 1913. Since that time X-ray crystallography has been used to investigate the structure of matter on an atomic scale. With the advent of automated spectrogoniometers and digital computers, structures of relatively great size and complexity, such as hemoglobin and myoglobin, have been examined by means of X-ray crystallography.

Of the various analytical tools available to the chemist, crystallography is the only one that gives a complete three-dimensional picture of the molecule. The detailed molecular structure, in turn, is often necessary for an understanding of the physical, chemical and biological properties of substances occurring in living organisms. Various amino acids, hormones, enzymes and proteins have been studied by means of X-ray crystallography. It was with the aid of this tool that the Watson-Crick model for DNA was developed. Since then, the molecular approach to biological systems has gained tremendously in favor.

This thesis concerns itself with the determination, by single-crystal X-ray diffraction, of the structures of three organic compounds. Since the methods of gathering the data, deriving structure factors, solving the structures by Patterson and Fourier techniques as well as the subsequent refinement by least-squares methods are adequately described in many reference books (1,2,3), they will not be described in detail in the thesis. The compounds analysed are listed in order of increasing difficulty and medical importance.

PART I

THE DETERMINATION OF THE STRUCTURE OF

DIBENZOTHIOPHENE

A. INTRODUCTION

In 1955 Burns and Iball (4) reported the crystal and molecular structure of fluorene, $C_{13}H_{10}$. Kurahashi et al (5) and Lahiri (6,7) determined the structure of carbazole, $C_{12}H_9N$, between 1966 and 1969. Finally, McCullough et al (8) reported the crystal and molecular structure of dibenzoselenophene, $C_{12}H_8Se$, in the winter of 1969. It seemed of interest therefore to determine the structure of dibenzothiophene $C_{12}H_8S$.

B. THE STRUCTURE OF DIBENZOTHIOPHENE

Experimental

When sublimed at atmospheric pressure in a stream of nitrogen, dibenzothiophene forms thin, colorless plates which are elongated along b, with (10$\bar{2}$) well developed and smaller (100) and (001) forms. The unit cell parameters and space group were determined from various photographic and diffractometer measurements.

Crystal data (λ, Mo-K_α = 0.7107 $\overset{o}{A}$).

Dibenzothiophene, $C_{12}H_8S$; M = 184.3; mp = 99°C.

Monoclinic, a = 8.67 $\pm$ 0.01, b = 6.00 $\pm$ 0.01, c = 18.70 $\pm$ 0.02 $\overset{o}{A}$,

β = 113.9 $\pm$ 0.1°.

U = 889.5 $\overset{o}{A}{}^3$. D_m = 1.35, Z = 4, D_x = 1.38.

F(000) = 384.

Absorption coefficient for X-rays, μ(Mo-K_α) = 2.99 cm^{-1}.

Absent reflexions: h0ℓ when ℓ is odd, 0k0 when k is odd.

Space group is $P2_1/c(C_{2h}^5)$.

The intensities of all reflexions with 2θ (Mo-K$_\alpha$)$<$ 50° (minimum d, 0.84 Å) were measured on a G.E. XRD 5 Spectrogoniometer, with single Crystal Orienter, using a scintillation counter, Mo-K$_\alpha$ radiation (zirconium filter and pulse height analyser), and the moving-crystal moving-counter technique of Furnas (9). All the intensities were corrected for background radiation (approximately only a function of θ) and the structure amplitudes were derived as usual. The crystal, a square plate measuring 0.58 x 0.53 x 0.20 mm was mounted with b parallel to the axis of the goniostat so that the cross section traversed by the X-ray was 0.58 x 0.20 mm. The following sources of error in the measured structure factors were considered. Firstly, taking the crystal as a cylinder with a mean diameter of 0.39 mm, μR is 0.058 and the absorption correction factor A* is 1.10 and constant over the range of θ = 0-25°; thus the maximum absorption error is negligible for the above range of θ . Secondly, absorption errors due to non-uniformity of crystal dimension were estimated by considering the shortest (0.20 mm) and the longest (0.8 mm) path lengths in the crystal. The absorption corrections for the corresponding structure factors are exp(2.99 x 0.02/2) and exp(2.99 x 0.08/2) or 1.03 and 1.13 respectively. Therefore, the maximum deviation from the mean correction is less than 5%. Since the total maximum error in F_o due to absorption is 5% and since most of the errors will be much smaller than this value, no corrections were made for absorption.

Structure Analysis

The position of the sulfur atom was determined from a three-dimensional Patterson synthesis (0.156, 0.167, 0.135) and structure factors were calculated for all the three-dimensional data for sulfur only, using scattering factors from the International Tables for X-ray Crystallography 1962 (10) and an isotropic thermal parameter of 4.0 $\overset{\circ}{A}{}^2$. One least-squares refinement reduced R to 0.56. A three-dimensional Fourier series summed with phases based on the sulfur atom revealed the positions of all the carbon atoms. When these were introduced into the structure factor calculations with scattering factors from the International Tables and B = 4.0 $\overset{\circ}{A}{}^2$, R dropped to 0.45. Further, refinement of the positional and isotropic thermal parameters together with an overall scale factor, proceeded by the method of block-diagonal least-squares, the function minimized being $\Sigma w(|F_o|-|F_c|)^2$. Since the structure factors were considered to be least accurately measured for the very strong reflexions which are affected most by absorption, and for the very weak and unobserved reflexions the intensities of which are close to that of background radiation, the weighting scheme employed was $\sqrt{w} = 1$ if $|F_o| < F^*$, $\sqrt{w} = |F_o|/F^*$ if $|F_o| \geq F^*$ where F^* was taken as 5. For unobserved reflexions $\sqrt{w}$ was 0.70.

After fourteen isotropic least-squares refinement cycles, R was 0.12 and shifts in positional and thermal parameters were small in magnitude and random in direction, the largest shift being less than one fourth of a standard deviation.

Further refinement commenced with anisotropic thermal parameters; seven anisotropic refinement cycles decreased R to 0.10. A three-dimensional difference synthesis summed at this stage of the analysis

revealed all eight hydrogen atoms (Figure 1). Their peak electron

densities varied between 0.4 and 1.0 e$\overset{\circ}{A}^{-3}$. When these hydrogen atoms

were introduced into the structure factor calculations with scattering

factors from the International Tables and B = 4.0 $\overset{\circ}{A}^{2}$, R fell to 0.09.

During the subsequent three least-squares cycles the shifts of the

isotropic thermal parameters of hydrogen atoms 1, 3, and 8 were large

and positive. A second difference synthesis was prepared in order to

determine the precise positions of hydrogens 1, 3, and 8. A final series

of five least-squares cycles completed the refinement. During the last

cycle, parameter shifts were small and nonsystematic, the largest

shift being one quarter of a standard deviation for the heavier atoms

and one half of a standard deviation for the hydrogen atoms.

The positional and thermal parameters of all the atoms as derived

from the final least-squares cycle are given in Table 1, together with

their standard deviations computed from the inverses of the diagonal

terms of the matrix of the least-squares normal equations. The atom

numbering used is shown in Figure 1. The hydrogen atoms were assigned

the numbers of the carbon atoms to which they are bonded. The final

three dimensional electron density distribution is shown in Figure 2;

all the heavier atoms are well resolved with peak densities of 10 e$\overset{\circ}{A}^{-3}$

for carbon atoms and 30 e$\overset{\circ}{A}^{-3}$ for the sulfur atom.

The final measured and calculated structure factors are listed in

Table 2; R is 0.083 for 1176 observed reflexions. A final three-

dimensional difference synthesis was computed and showed random fluctua-

tions in electron density as great as ± 0.6e$\overset{\circ}{A}^{-3}$.
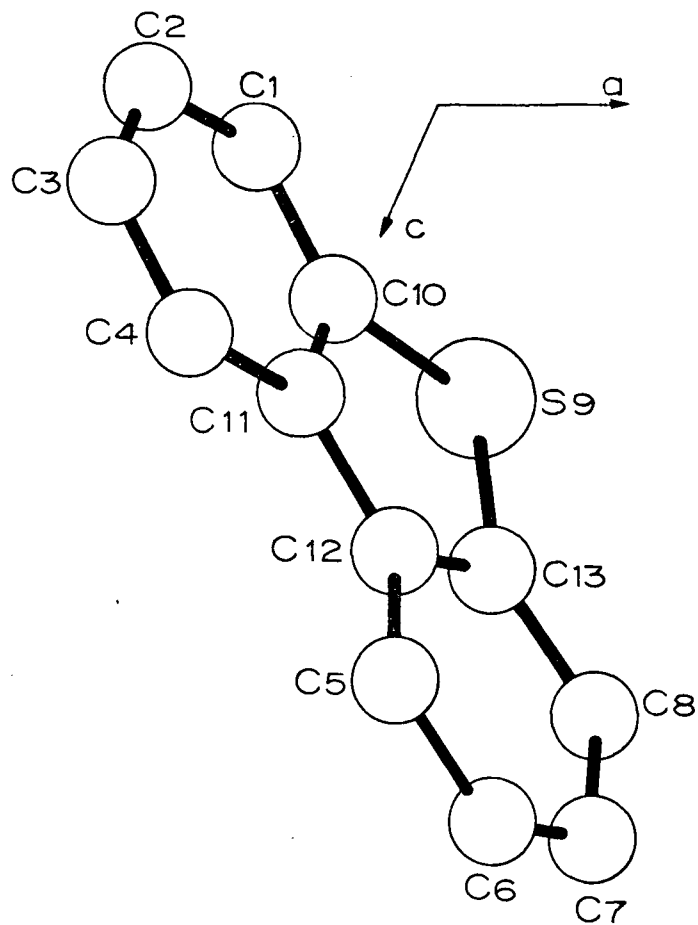
Figure 1. (a) Perspective drawing of molecule as
viewed along b showing atom numbering.
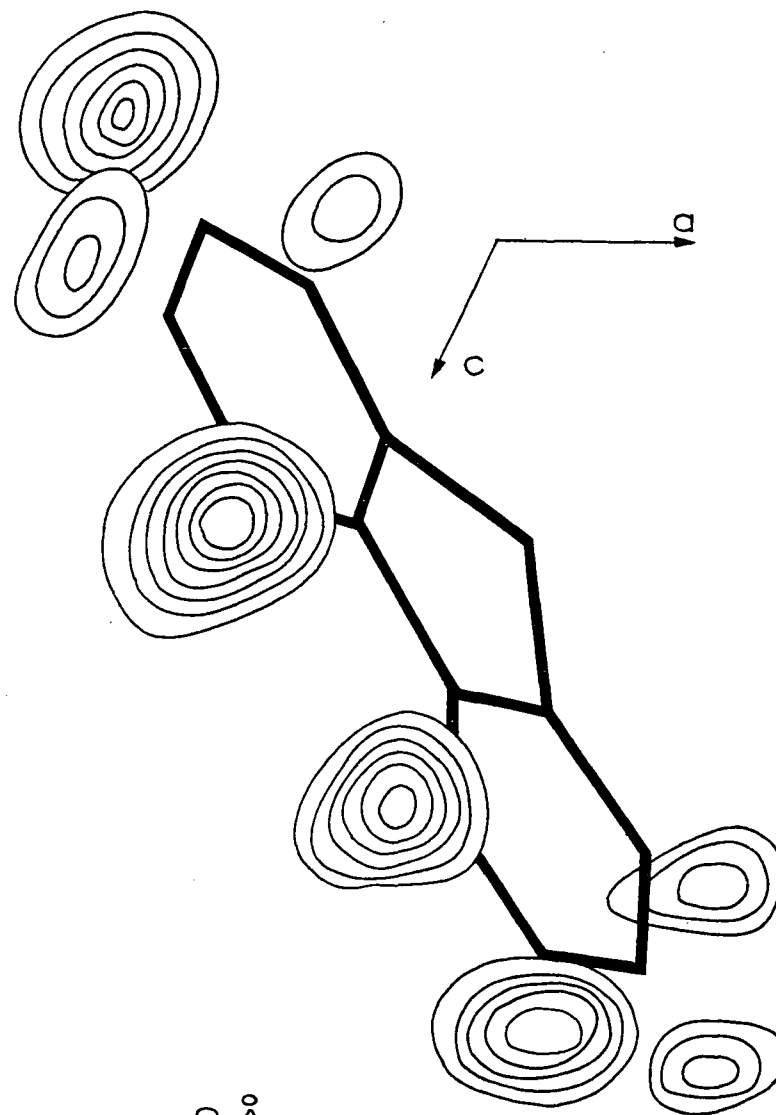
(b) Three-dimensional difference synthesis
projected along b. The hydrogen atoms have
the same number as the carbon atom to which
they are bonded.

Table 1

Final positional (fractional, $\times 10^4$ for C and S, $\times 10^3$ for H) and thermal ($\overset{\circ}{A}{}^2 \times 10^2$; B in $\overset{\circ}{A}{}^2$) parameters, with standard deviations in parentheses.

Atom	x	y	z	
C(1)	−1496(11)	3036(16)	0192(5)	
C(2)	−2755(11)	4659(17)	−0087(5)	
C(3)	−2693(12)	6565(17)	0346(5)	
C(4)	−1380(10)	6938(14)	1047(5)	
C(5)	1934(10)	6997(14)	2652(5)	
C(6)	3393(11)	6675(15)	3314(5)	
C(7)	4362(10)	4800(17)	3379(5)	
C(8)	3905(11)	3197(15)	2808(5)	
S(9)	1542(3)	1674(4)	1361(1)	
C(10)	−0163(10)	3435(14)	0903(5)	
C(11)	−0082(8)	5383(13)	1336(4)	
C(12)	1403(9)	5405(13)	2060(4)	
C(13)	2416(9)	3499(13)	2151(4)	

Atom	x	y	z	B
H(1)	−160(22)	173(32)	−023(11)	9(5)
H(2)	−381(11)	409(32)	−058(5)	2(2)
H(3)	−346(15)	782(23)	011(8)	5(3)
H(4)	−126(11)	846(14)	127(5)	1(2)
H(5)	129(11)	823(14)	254(5)	1(2)
H(6)	353(10)	790(16)	357(5)	1(2)
H(7)	531(11)	454(16)	388(5)	2(2)
H(8)	463(15)	209(24)	275(7)	5(3)

Atom	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}	Mean $\sigma(U)$
C(1)	5.33	−0.49	1.50	6.03	−0.58	3.49	0.38
C(2)	4.69	−0.60	0.76	6.39	0.17	4.06	0.40
C(3)	4.60	0.51	1.59	6.02	0.73	5.01	0.40
C(4)	4.21	0.32	1.88	4.24	0.04	4.69	0.33
C(5)	4.63	−0.04	1.75	4.56	−0.05	4.01	0.33
C(6)	4.40	−1.05	1.38	5.15	−0.83	4.31	0.36
C(7)	3.87	−0.91	1.34	6.74	0.49	4.61	0.38
C(8)	4.19	0.43	1.51	5.19	0.78	4.80	0.37
C(9)	5.23	0.75	1.49	4.49	−0.63	4.84	0.09
C(10)	4.62	0.03	1.71	4.67	−0.14	3.55	0.32
C(11)	3.10	0.04	1.56	3.95	0.29	3.72	0.28
C(12)	3.44	−0.58	1.28	3.88	−0.14	3.23	0.28
C(13)	3.28	0.01	1.59	4.08	0.32	4.26	0.31
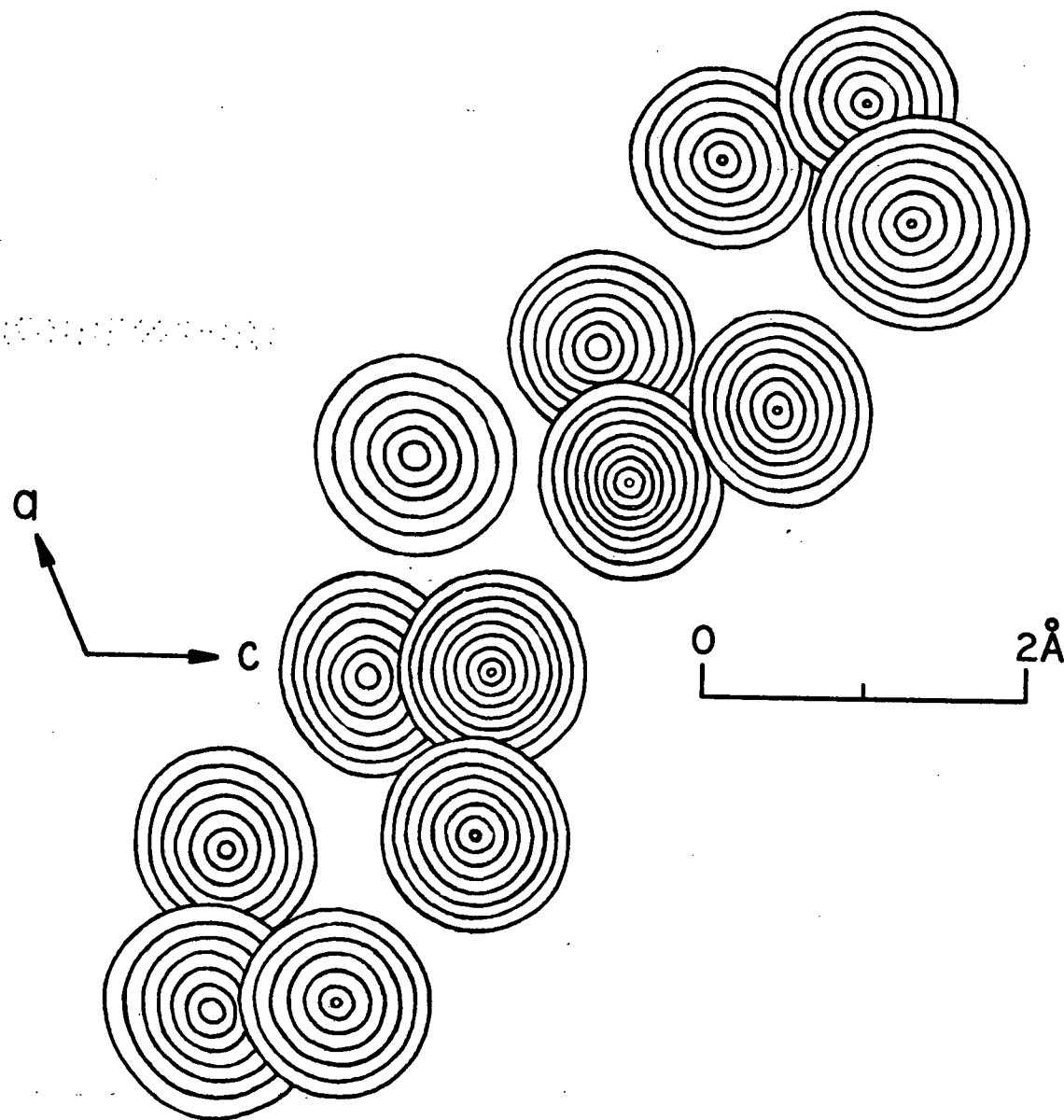
Figure 2.   Electron-density distribution projected along b.   Contours are at intervals of 1 e$\mathring{A}^{-3}$ for carbon and at 5 e$\mathring{A}^{-3}$ starting at 5 e$\mathring{A}^{-3}$ for sulfur.

Table 2

Measured and calculated structure factors (Unobserved reflexions are indicated by a negative sign in front of $|F_o|$).

h	k	ℓ	$\lvert F_o\rvert$	F_c
1	0	0	68.8	66.5
2	0	0	53.4	-49.1
3	0	0	47.8	-39.7
4	0	0	34.5	-22.7
5	0	0	27.3	17.7
6	0	0	29.6	24.5
7	0	0	37.4	32.7
8	0	0	24.2	13.3
9	0	0	-1.8	-3.0
0	0	2	40.9	-32.9
1	0	-2	27.3	21.8
1	0	2	19.2	16.7
2	0	-2	57.0	55.4
2	0	2	58.4	-58.1
3	0	-2	2.3	2.2
3	0	2	38.4	34.0
4	0	-2	-1.0	-3.0
4	0	2	35.9	36.2
5	0	-2	44.5	-42.3
5	0	2	3.7	2.0
6	0	-2	10.6	-9.7
6	0	2	6.4	6.2
7	0	-2	10.0	[illegible]
7	0	2	[illegible]	[illegible]
8	0	-2	8.7	7.6
8	0	2	4.6	-4.5
9	0	-2	-1.7	-2.4
9	0	2	5.5	-5.9
0	0	4	21.8	-17.3
1	0	-4	65.5	-73.0
1	0	4	18.4	-17.5
2	0	-4	135.9	-146.2
2	0	4	9.5	10.2
3	0	-4	25.1	28.6
3	0	4	9.4	-6.7
4	0	-4	21.8	22.0
4	0	4	14.6	14.0
5	0	-4	4.0	-2.9
5	0	4	11.7	-10.7
6	0	-4	20.0	-19.5
6	0	4	29.6	-31.1
7	0	-4	14.6	-13.1
7	0	4	13.8	-14.3
8	0	-4	12.6	-11.7
8	0	4	6.8	6.5
9	0	-4	18.4	-16.9
10	0	-4	-1.8	2.5
0	0	6	40.5	33.8
1	0	-6	52.4	-50.7
1	0	6	6.0	6.6
2	0	-6	28.3	-26.1
2	0	6	5.3	-7.0
3	0	-6	-0.9	-5.0
3	0	6	4.5	2.8
4	0	-6	5.5	9.3
4	0	6	21.7	-22.0
5	0	-6	6.3	7.3
5	0	6	23.2	-24.0
6	0	-6	9.5	6.6
6	0	6	-1.3	1.9
7	0	-6	4.8	3.9
7	0	6	11.0	11.5
8	0	-6	13.5	-13.8
9	0	-6	7.7	3.2
10	0	-6	-1.5	2.5
0	0	8	58.8	51.6
1	0	-8	33.5	31.2
1	0	8	35.2	34.0
2	0	-8	10.4	8.1
2	0	8	25.7	-25.7
3	0	-8	17.2	-17.9
3	0	8	29.0	-28.6
4	0	-8	20.9	-19.6
4	0	8	-1.2	0.6
5	0	-8	9.2	-9.8
5	0	8	14.3	13.7
6	0	-8	30.4	30.8
6	0	8	6.2	5.7
7	0	-8	23.0	23.1
7	0	8	7.6	6.8
8	0	-8	13.2	13.2
9	0	-8	5.6	-9.5
10	0	-8	5.7	-4.6
0	0	10	-1.2	-1.4
1	0	-10	15.5	18.8
1	0	10	6.2	-6.1
2	0	-10	7.3	7.5
2	0	10	6.5	-6.7
3	0	-10	5.8	6.5
3	0	10	6.0	5.2
4	0	-10	-1.2	2.1
4	0	10	6.4	4.9
5	0	-10	16.8	-13.2
5	0	10	-1.4	-0.6
6	0	-10	17.6	-17.2
6	0	10	-1.5	0.8
7	0	-10	5.3	7.8
8	0	-10	12.3	11.2
9	0	-10	7.3	6.3
10	0	-10	-1.8	3.1
0	0	12	26.7	-15.5
1	0	-12	32.2	-32.3
1	0	12	-1.1	-0.1
2	0	-12	16.7	-18.1
2	0	12	24.8	27.2
3	0	-12	15.0	19.0
3	0	12	15.6	15.1
4	0	-12	14.3	14.9
4	0	12	-1.3	2.1
5	0	-12	15.8	17.0
5	0	12	11.0	-10.6
6	0	-12	13.5	9.9
7	0	-12	13.2	-12.3
8	0	-12	21.7	-23.4
9	0	-12	10.5	-4.2
10	0	-12	-1.8	2.1
0	0	14	23.7	19.1
1	0	-14	14.8	-15.1
1	0	14	25.5	26.9
2	0	-14	18.2	-17.7
2	0	14	6.8	7.5
3	0	-14	25.7	-23.9
3	0	14	-1.4	2.2
4	0	-14	13.9	13.4
4	0	14	12.0	-11.5
5	0	-14	27.5	27.6
6	0	-14	8.3	8.1
7	0	-14	7.7	-1.1
8	0	-14	-1.6	0.3
9	0	-14	9.3	-7.9
0	0	16	15.2	-9.5
1	0	-16	30.0	29.8
1	0	16	14.7	-15.7
2	0	-16	11.5	12.4
2	0	16	8.4	-8.9
3	0	-16	5.3	-5.0
3	0	16	-1.5	-2.3
4	0	-16	16.9	-14.7
5	0	-16	17.8	-17.6
6	0	-16	-1.5	-1.2
7	0	-16	-1.6	2.4
8	0	-16	-1.7	1.8
9	0	-16	-1.8	1.8
0	0	18	12.5	-5.7
1	0	-18	17.3	-17.7
1	0	18	12.0	-12.6
2	0	-18	7.5	-8.1
2	0	18	3.3	2.7
3	0	-18	11.7	9.7
4	0	-18	3.8	4.8
5	0	-18	-1.6	1.4
6	0	-18	18.5	-18.0
7	0	-18	12.0	-12.5
8	0	-18	-1.7	0.7
0	0	20	9.8	-3.3
1	0	-20	3.2	-0.1
2	0	-20	3.1	-1.0
3	0	-20	13.9	-12.5
4	0	-20	7.6	7.4
5	0	-20	11.0	10.5
6	0	-20	5.0	4.6
7	0	-20	-1.8	-0.6
3	0	-22	3.7	3.6
4	0	-22	8.5	10.0
5	0	-22	9.4	9.4
1	1	0	39.8	-38.3
2	1	0	16.4	-17.3
3	1	0	3.5	-3.7
4	1	0	18.1	17.9
5	1	0	5.1	4.4
6	1	0	10.8	11.1
7	1	0	10.3	9.6
8	1	0	11.8	-10.6
9	1	0	8.4	-6.4
0	1	1	41.6	-35.3
1	1	-1	50.9	-55.3
1	1	1	4.5	-3.8
2	1	-1	36.9	36.1
2	1	1	15.1	-14.5
3	1	-1	31.2	-30.1
3	1	1	21.8	-20.0
4	1	-1	17.4	-16.7
4	1	1	29.7	-24.1
5	1	-1	3.5	-4.8
5	1	1	7.1	7.4
6	1	-1	-1.3	1.0
6	1	1	-1.4	1.6
7	1	-1	-1.5	-0.6
7	1	1	10.0	-10.6
8	1	-1	-1.6	-2.4
8	1	1	10.5	-11.1
9	1	-1	-1.8	2.0
9	1	1	-1.8	-0.6
0	1	2	50.1	-46.9
1	1	-2	29.0	29.4
1	1	2	23.7	-22.4
2	1	-2	17.4	-17.6
2	1	2	14.6	14.3
3	1	-2	5.4	4.6
3	1	2	23.6	23.5
4	1	-2	15.5	-17.1
4	1	2	-1.0	0.6
5	1	-2	10.8	10.5
5	1	2	6.3	-5.1
6	1	-2	21.4	21.4
6	1	2	14.5	-15.1
7	1	-2	-1.5	-2.1
7	1	2	7.9	-8.0
8	1	-2	-1.6	2.6
8	1	2	5.8	5.5
9	1	-2	-1.7	2.1
0	1	3	50.7	-48.3
1	1	-3	65.0	85.1
1	1	3	6.4	-6.9
2	1	-3	50.3	55.9
2	1	3	3.5	-3.3
3	1	-3	15.3	15.1
3	1	3	5.9	6.0
4	1	-3	-1.1	1.2
4	1	3	17.0	16.3
5	1	-3	-1.2	-0.3
5	1	3	11.2	11.1
6	1	-3	3.2	2.6
6	1	3	4.9	4.0
7	1	-3	5.8	-5.3
7	1	3	6.3	-5.5
8	1	-3	15.0	14.3
8	1	3	-1.7	-0.3
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8	1	4	7.2	7.6
9	1	-4	-1.7	2.8
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5	1	6	3.5	-2.3
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9	1	-6	12.1	12.1
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4	1	-7	18.7	-16.5
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6	1	-8	22.0	23.5
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10	1	-8	6.8	-5.9
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1	1	-9	18.2	18.0
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2	1	-9	24.8	25.4
2	1	9	13.1	-13.5
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2	1	-19	11.1	11.1
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7	1	-19	-1.7	-0.4
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7	2	-14	8.6	10.1
8	2	-14	7.5	8.0
9	2	-14	4.9	4.9
0	2	15	6.6	6.6
1	2	-15	18.1	-19.3
1	2	15	14.8	-16.0
2	2	-15	12.7	-12.3
2	2	15	6.5	-7.8
3	2	-15	4.0	-4.3
3	2	15	3.5	3.2
4	2	-15	-1.5	2.9
5	2	-15	10.4	10.1
6	2	-15	10.4	10.9
7	2	-15	-1.6	-1.0
8	2	-15	10.2	-9.5
9	2	-15	6.4	-5.3
0	2	16	4.9	4.1
1	2	-16	2.8	-1.8
1	2	16	5.3	4.6
2	2	-16	3.5	-3.8
2	2	16	3.5	2.0
3	2	-16	10.5	11.1
4	2	-16	8.3	9.2
5	2	-16	6.1	5.5
6	2	-16	5.5	-5.2
7	2	-16	4.8	-3.5
8	2	-16	7.9	6.9
0	2	17	8.8	-8.4
1	2	-17	7.2	8.2
1	2	17	-1.4	0.9
2	2	-17	5.4	7.1
2	2	17	4.7	5.0
3	2	-17	-1.6	2.7
4	2	-17	2.9	-3.1
5	2	-17	3.9	-3.7
6	2	-17	-1.6	1.9
7	2	-17	11.4	11.2
8	2	-17	7.0	5.9
0	2	19	4.1	2.5
1	2	-18	-1.7	1.0
1	2	18	-1.5	-0.6
2	2	-18	6.7	-7.0
3	2	-18	9.5	-11.1
4	2	-18	-1.6	-2.0
5	2	-18	-1.6	3.4
6	2	-18	-1.7	2.0
7	2	-18	4.8	4.0
8	2	-18	6.2	-7.8
0	2	19	4.5	4.5
1	2	-19	3.1	3.6
2	2	-19	10.9	11.4
3	2	-19	9.0	10.1
4	2	-19	-1.7	1.9
5	2	-19	5.3	-5.8
6	2	-19	-1.7	-1.7
7	2	-19	-1.8	-3.7
1	2	-20	4.0	3.7
2	2	-20	3.2	1.3
3	2	-20	-1.7	-1.4
4	2	-20	3.9	-3.4
5	2	-20	8.4	-9.2
6	2	-20	4.0	-3.3
3	2	-21	6.3	5.8
4	2	-21	-1.8	-1.1
5	2	-21	-1.8	-0.4

Table 2 (Continued)

1	3	0	-1.1	1.7
2	3	0	-1.1	-0.6
3	3	0	-1.2	4.0
4	3	0	2.4	2.5
5	3	0	5.1	-4.9
6	3	0	-1.5	-2.6
7	3	0	-1.6	-2.4
8	3	0	-1.8	2.4
0	3	1	6.3	-6.3
1	3	-1	10.3	-11.2
1	3	1	3.8	3.9
2	3	-1	26.7	-26.5
2	3	1	41.3	41.8
3	3	-1	12.7	-10.9
3	3	1	20.0	20.2
4	3	-1	24.3	24.1
4	3	1	-1.3	-2.1
5	3	-1	12.6	13.6
5	3	1	12.6	-13.8
6	3	-1	8.9	8.6
6	3	1	24.4	-25.7
7	3	-1	7.8	-7.1
7	3	1	6.4	4.9
8	3	-1	9.3	-10.1
8	3	1	11.0	10.4
0	3	2	12.8	11.0
1	3	-2	3.6	3.7
1	3	2	6.2	5.7
2	3	-2	8.7	-9.3
2	3	2	-1.0	-0.3
3	3	-2	10.0	-10.7
3	3	2	6.4	-6.6
4	3	-2	4.0	-4.3
4	3	2	4.4	3.9
5	3	-2	4.2	3.4
5	3	2	8.5	9.8
6	3	-2	-1.5	-1.0
6	3	2	5.9	5.5
7	3	-2	-1.6	-1.7
7	3	2	-1.7	3.3
8	3	-2	-1.7	-0.6
8	3	2	-1.8	-2.5
0	3	3	38.8	38.5
1	3	-3	15.5	-15.9
1	3	3	60.4	60.7
2	3	-3	25.5	-26.5
2	3	3	4.1	4.5
3	3	-3	14.9	-12.5
3	3	3	14.7	-14.2
4	3	-3	11.2	-11.1
4	3	3	29.2	-30.3
5	3	-3	10.3	10.0
5	3	3	-1.2	-1.0
6	3	-3	22.4	21.7
6	3	3	18.8	19.0
7	3	-3	8.3	8.5
7	3	3	6.4	6.2
8	3	-3	-1.7	-3.4
9	3	-3	10.1	-9.0
0	3	4	7.6	-5.2
1	3	-4	-1.1	2.7
1	3	4	5.9	-9.3
2	3	-4	6.3	-6.6
2	3	4	14.1	-13.1
3	3	-4	-1.2	-0.5
3	3	4	6.6	5.8
4	3	-4	3.9	4.8
4	3	4	6.7	7.0
5	3	-4	3.7	4.4
5	3	4	3.3	2.7
6	3	-4	-1.5	1.8
6	3	4	5.3	-4.5
7	3	-4	-1.5	1.1
7	3	4	4.2	-3.6
8	3	-4	-1.7	0.2
9	3	-4	-1.8	3.3
0	3	5	8.7	-6.9
1	3	-5	17.5	19.6
1	3	5	13.0	-13.7
2	3	-5	11.0	11.7
2	3	5	22.3	-22.4
3	3	-5	4.1	-4.6
3	3	5	19.5	-19.7
4	3	-5	21.2	-22.5
4	3	5	25.5	25.5
5	3	-5	11.4	-11.4
5	3	5	8.3	8.5
6	3	-5	4.2	-4.7
6	3	5	-1.4	-0.7
7	3	-5	4.3	3.4
7	3	5	-1.5	-1.0
8	3	-5	5.1	4.5
9	3	-5	-1.6	-0.5
0	3	6	5.3	4.8
1	3	-6	3.0	-3.6
1	3	6	4.9	4.4
2	3	-6	6.7	7.0
2	3	6	4.8	-6.9
3	3	-6	-1.2	0.9
3	3	6	17.0	-15.8
4	3	-6	9.7	12.2
4	3	6	7.0	-6.6
5	3	-6	5.5	9.7
5	3	6	4.4	-3.4
6	3	-6	7.1	3.1
6	3	6	4.5	2.5
7	3	-6	4.5	-4.3
7	3	6	-1.5	1.8
8	3	-6	-1.7	-1.8
9	3	-6	-1.8	-0.8
0	3	7	25.8	-25.9
1	3	-7	26.8	-26.6
1	3	7	18.7	-18.2
2	3	-7	13.7	15.2
2	3	7	2.9	3.3
3	3	-7	10.2	10.2
3	3	7	3.8	-3.7
4	3	-7	2.9	-2.8
4	3	7	9.1	-9.2
5	3	-7	12.6	-13.5
5	3	7	8.9	8.8
6	3	-7	12.2	-12.1
6	3	7	9.8	-8.4
7	3	-7	5.2	-5.2
8	3	-7	4.5	-7.8
9	3	-7	4.5	3.8
0	3	8	12.9	9.1
1	3	-8	-1.7	0.2
1	3	8	-1.1	-1.1
2	3	-8	6.7	-7.6
2	3	8	4.0	-3.7
3	3	-8	8.2	-8.4
3	3	8	-1.2	1.1
4	3	-8	3.8	-3.0
4	3	8	5.5	4.5
5	3	-9	-1.4	1.7
5	3	8	3.4	3.0
6	3	-8	-1.5	-0.6
6	3	8	-1.5	-2.0
7	3	-8	3.8	-4.1
8	3	-8	-1.7	-2.3
9	3	-8	-1.8	-1.9
0	3	9	9.4	-6.4
1	3	-9	16.9	-17.9
1	3	9	24.9	25.8
2	3	-9	12.1	-12.6
2	3	9	7.0	7.5
3	3	-9	10.9	6.8
3	3	9	-1.2	1.1
4	3	-9	11.8	13.2
4	3	9	6.6	-6.1
5	3	-9	4.8	5.1
5	3	9	9.7	-9.6
6	3	-9	14.3	15.5
7	3	-9	3.8	-4.5
8	3	-9	4.1	-3.5
9	3	-9	-1.8	2.0
0	3	10	7.9	7.9
1	3	-10	-1.3	-0.1
1	3	10	14.4	15.1
2	3	-10	7.8	8.1
2	3	10	3.5	3.8
3	3	-10	4.6	4.7
3	3	10	-1.3	0.6
4	3	-10	4.0	-4.4
4	3	10	-1.4	0.4
5	3	-10	6.7	-6.0
5	3	10	-1.5	0.1
6	3	-10	11.3	-12.1
7	3	-10	-1.6	-3.1
8	3	-10	-1.7	2.3
9	3	-10	-1.8	3.7
0	3	11	23.9	24.5
1	3	-11	9.8	10.7
1	3	11	26.9	27.8
2	3	-11	2.5	-2.5
2	3	11	14.4	15.5
3	3	-11	14.3	-15.7
3	3	11	13.7	-13.7
4	3	-11	16.9	-18.5
4	3	11	6.4	-7.2
5	3	-11	28.2	30.7
5	3	11	-1.5	1.0
6	3	-11	26.6	27.1
7	3	-11	10.0	10.1
8	3	-11	-1.7	-1.2
9	3	-11	6.8	-6.2
0	3	12	-1.7	0.8
1	3	-12	-1.4	0.8
1	3	12	5.1	-4.1
2	3	-12	-1.4	-0.4
2	3	12	5.8	-5.8
3	3	-12	3.4	-3.8
3	3	12	5.5	-3.4
4	3	-12	9.1	8.6
4	3	12	-1.4	2.2
5	3	-12	10.6	10.3
6	3	-12	-1.6	5.7
7	3	-12	4.2	-3.2
8	3	-12	-1.7	-1.5
9	3	-12	-1.8	3.0
0	3	13	8.0	-7.4
1	3	-13	5.3	4.4
1	3	13	2.5	-3.0
2	3	-13	19.9	22.5
2	3	13	-1.3	-0.6
3	3	-13	3.5	4.0
3	3	13	-1.4	-0.7
4	3	-13	4.3	-3.3
4	3	13	4.1	4.2
5	3	-13	18.0	-18.4
6	3	-13	6.4	-6.1
7	3	-13	9.3	9.2
8	3	-13	-1.7	-0.2
0	3	14	-1.3	-0.1
1	3	-14	4.8	5.4
1	3	14	-1.3	-0.4
2	3	-14	3.3	3.0
2	3	14	4.8	-3.8
3	3	-14	-1.5	2.3
3	3	14	-1.5	-2.2
4	3	-14	-1.5	-2.1
5	3	-14	-1.6	1.3
6	3	-14	-1.6	2.3
7	3	-14	-1.7	2.4
8	3	-14	5.3	4.9
0	3	15	18.0	-19.5
1	3	-15	14.9	-15.7
1	3	15	7.1	-8.1
2	3	-15	6.6	-7.8
2	3	15	4.4	4.5
3	3	-15	11.2	8.0
4	3	-15	5.1	5.5
5	3	-15	3.6	4.5
6	3	-15	5.4	-2.9
7	3	-15	26.2	-28.0
8	3	-15	10.6	-11.1
0	3	16	6.0	4.3
1	3	-16	-1.6	-1.4
1	3	16	5.3	4.7
2	3	-16	-1.6	-0.2
2	3	16	-1.5	0.2
3	3	-16	-1.6	-2.7
4	3	-16	-1.6	1.0
5	3	-16	-1.6	2.7
6	3	-16	4.6	-4.2
7	3	-16	6.1	-5.2
8	3	-16	-1.8	-4.6
0	3	17	4.6	-3.9
1	3	17	10.5	10.1
2	3	-17	3.4	-3.1
3	3	-17	6.5	-6.9
4	3	-17	4.2	-5.5
5	3	-17	7.9	8.0
6	3	-17	-1.7	1.7
7	3	-17	-1.8	3.0
0	3	18	4.7	4.1
1	3	-18	-1.7	-0.2
2	3	-18	-1.7	2.8
3	3	-18	-1.7	1.4
4	3	-18	-1.7	-1.2
5	3	-18	4.2	-4.6
6	3	-18	3.6	-2.8
7	3	-18	-1.8	-1.6
3	3	-20	-1.8	1.1
1	3	-19	10.7	10.9
2	3	-19	-1.8	0.7
3	3	-19	6.6	-6.8
4	3	-19	-1.8	-1.0
5	3	-19	-1.9	1.3
6	3	-19	6.6	6.0
4	3	-20	-1.8	2.1
0	4	0	10.7	-9.6
1	4	0	6.7	-6.1
2	4	0	9.6	8.6
3	4	0	-1.4	1.3
4	4	0	-1.4	1.7
5	4	0	-1.5	0.6
6	4	0	-1.6	-1.1
7	4	0	-1.7	1.3
0	4	1	10.0	9.8
1	4	-1	-1.3	-0.9
1	4	1	-1.1	2.2
2	4	-1	26.4	26.3
2	4	1	-1.1	1.5
3	4	-1	27.6	27.5
3	4	1	10.0	-4.9
4	4	-1	-1.4	0.7
4	4	1	15.2	-16.5
5	4	-1	6.6	-6.2
5	4	1	10.8	-11.4
6	4	-1	6.2	-5.9
6	4	1	10.9	11.4
7	4	-1	5.2	5.1
7	4	1	6.2	5.9
0	4	2	-1.0	1.3
1	4	-2	10.0	-9.9
1	4	2	4.8	6.2
2	4	-2	14.1	-15.2
2	4	2	3.5	2.4
3	4	-2	3.7	-3.9
3	4	2	4.8	4.9
4	4	-2	9.1	9.4
4	4	2	9.2	-8.0
5	4	-2	-1.5	1.0
5	4	2	4.7	-4.2
6	4	-2	-1.6	2.3
6	4	2	7.0	-6.1
7	4	-2	-1.7	-2.2
7	4	2	-1.9	-1.7
8	4	-2	-1.8	-0.4
0	4	3	14.6	14.2
1	4	-3	4.7	-4.6
1	4	3	6.0	-6.7
2	4	-3	4.8	5.7
2	4	3	14.3	-14.4
3	4	-3	16.6	17.8
3	4	3	10.9	-11.4
4	4	-3	14.2	18.7
4	4	3	11.4	-11.4
5	4	-3	6.4	6.1
5	4	3	4.5	-4.0
6	4	-3	-1.6	0.7
6	4	3	-1.4	-1.7
7	4	-3	5.3	-5.6
7	4	3	5.2	4.5
8	4	-3	12.3	-12.3
0	4	4	18.7	8.3
1	4	-4	14.0	14.5
1	4	4	-1.1	2.1
2	4	-4	2.9	-4.4
2	4	4	4.8	-5.1
3	4	-4	12.2	-13.2
3	4	4	4.4	-4.2
4	4	-4	14.1	-13.1
4	4	4	10.4	-7.4
5	4	-4	5.3	5.6
5	4	4	9.1	-9.1
6	4	-4	7.5	7.2
6	4	4	7.4	6.9
7	4	-4	-1.7	2.6
8	4	-4	-1.8	1.7
0	4	5	21.0	-21.0
1	4	-5	12.3	-12.0
1	4	5	14.2	-14.5
2	4	-5	11.2	-12.2
2	4	5	-1.2	-0.3
3	4	-5	6.4	-6.6
3	4	5	17.7	18.4
4	4	-5	18.2	-19.0
4	4	5	14.3	14.8
5	4	-5	4.3	-4.6
5	4	5	-1.4	-1.0
6	4	-5	9.0	8.8
6	4	5	3.8	-3.9
7	4	-5	-1.7	1.7
8	4	-5	-1.8	-1.1
0	4	6	3.4	3.0
1	4	-6	7.0	6.9
1	4	6	8.5	-8.9
2	4	-6	13.8	14.2
2	4	6	-1.2	-0.7
3	4	-6	12.9	13.0
3	4	6	-1.3	0.4
4	4	-6	6.5	6.7
4	4	6	9.8	8.6
5	4	-6	5.1	-5.3
5	4	6	7.2	7.4
6	4	-6	11.1	-11.4
6	4	6	-1.5	1.8
7	4	-6	4.3	5.3
8	4	-6	6.5	6.7
0	4	7	6.9	-6.6
1	4	-7	26.7	27.4
1	4	7	6.9	7.7
2	4	-7	20.4	21.2
2	4	7	30.2	31.4
3	4	-7	21.2	-22.9
3	4	7	16.8	17.1
4	4	-7	25.9	-27.0
4	4	7	-1.4	-2.2
5	4	-7	15.1	-15.5
5	4	7	9.9	-9.5
6	4	-7	-1.6	-0.4
7	4	-7	9.9	9.2
8	4	-7	6.7	5.9
0	4	8	-1.2	0.5
1	4	-8	-1.4	-1.5
1	4	8	2.4	-2.7
2	4	-8	5.2	-6.2
2	4	8	7.6	6.5
3	4	-8	-1.4	-2.0
3	4	8	18.7	18.6
4	4	-8	15.5	16.8
4	4	8	-1.4	1.8
5	4	-8	9.0	9.0
5	4	8	-1.5	-2.3
6	4	-8	-1.6	1.5
7	4	-8	7.5	-7.7
8	4	-8	5.1	-4.7
0	4	9	15.5	15.5
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1	4	9	5.9	5.1
2	4	-9	-1.4	-2.3
2	4	9	14.4	-15.7
3	4	-9	22.2	23.4
3	4	9	5.3	-5.1
4	4	-9	7.6	8.4
4	4	9	3.2	-3.3
5	4	-9	6.1	-5.4
5	4	9	-1.5	0.3
6	4	-9	-1.6	-2.1
7	4	-9	-1.7	-1.3
8	4	-9	-1.8	1.4
0	4	10	5.8	3.8
1	4	-10	2.6	-2.1
1	4	10	7.1	6.6
2	4	-10	13.4	-15.0
2	4	10	-1.3	-0.4
3	4	-10	7.9	-7.8
3	4	10	4.3	-4.4
4	4	-10	8.1	-8.4
4	4	10	7.2	-6.4
5	4	-10	3.2	-2.8
6	4	-10	-1.6	1.2
7	4	-10	-1.7	2.2
8	4	-10	-1.8	1.7
0	4	11	10.8	-10.8
1	4	-11	11.0	-11.2
1	4	11	8.7	-8.7
2	4	-11	8.9	-8.9
2	4	11	-1.4	-1.6
3	4	-11	9.5	-9.5
3	4	11	4.6	-4.7
4	4	-11	3.1	2.6
4	4	11	4.5	4.4
5	4	-11	15.8	16.5
6	4	-11	7.0	7.0
7	4	-11	-1.7	-1.7
8	4	-11	5.9	-6.4
0	4	12	4.8	4.3
1	4	-12	3.7	3.8
1	4	12	12.7	-11.6
2	4	-12	3.1	-3.9
2	4	12	8.5	-8.8
3	4	-12	7.0	-7.1
3	4	12	-1.5	-3.1
4	4	-12	4.8	-2.4
5	4	-12	2.9	-2.4
6	4	-12	8.9	-9.6
7	4	-12	-1.7	2.1
8	4	-12	-1.8	2.2
0	4	13	-1.3	-0.5
1	4	-13	6.4	7.3
1	4	13	5.5	-5.3
2	4	-13	-1.6	-1.4
2	4	13	4.1	3.6
3	4	-13	6.6	-6.9
3	4	13	9.0	9.5
4	4	-13	-1.6	-1.7
5	4	-13	3.6	-3.8
6	4	-13	4.1	3.6
7	4	-13	-1.9	0.4
0	4	14	6.3	-3.1
1	4	-14	-1.6	-1.1
1	4	14	2.5	-2.3
2	4	-14	-1.6	2.6
2	4	14	-1.5	1.4
3	4	-14	6.1	6.5
4	4	-14	8.6	9.5
5	4	-14	-1.7	-2.3
6	4	-14	-1.7	1.4
7	4	-14	-1.8	1.1
0	4	15	12.7	-9.6
1	4	-15	11.3	12.1
1	4	15	6.9	6.9
2	4	-15	4.3	5.0
3	4	-15	-1.6	1.5
4	4	-15	7.2	-7.6
5	4	-15	5.6	-6.0
6	4	-15	-1.7	-1.4
7	4	-15	9.0	9.2
0	4	16	-1.5	3.9
1	4	-16	-1.7	0.2
2	4	-16	4.1	-4.7
3	4	-16	4.6	5.6
4	4	-16	7.4	7.6
5	4	-16	5.3	5.6
6	4	-16	3.2	0.4
1	4	-17	3.6	-3.3
2	4	-17	-1.7	1.1
3	4	-17	3.5	4.3
4	4	-17	4.8	5.9
5	4	-17	-1.8	-0.7
6	4	-17	-1.8	-2.8
2	4	-18	-1.8	-1.8
3	4	-18	4.6	-4.7
4	4	-18	-1.9	-2.0
5	4	-18	-1.8	1.2
1	5	0	22.6	22.6
2	5	0	16.3	16.4
3	5	0	4.6	-4.1
4	5	0	8.7	-8.8
5	5	0	-1.7	-7.3
6	5	0	9.2	-8.6
0	5	1	-1.2	-1.4
1	5	-1	5.5	-5.3
1	5	1	4.0	-3.5
2	5	-1	9.2	9.6
2	5	1	11.2	-10.4
3	5	-1	-1.5	-1.8
3	5	1	-1.5	-1.1
4	5	-1	-1.6	-1.5
4	5	1	-1.6	-2.0
5	5	-1	-1.6	-0.7
5	5	1	6.1	5.8
6	5	-1	3.5	-3.1
6	5	1	-1.8	3.6
0	5	2	26.9	27.2
1	5	-2	17.6	-16.7
1	5	2	11.1	11.2
2	5	-2	10.1	-9.4
2	5	2	5.4	-5.3
3	5	-2	-1.5	1.8
3	5	2	9.1	-9.0
4	5	-2	9.6	8.9
4	5	2	-1.4	1.9
5	5	-2	-1.6	-1.5
5	5	2	7.9	7.2
6	5	-2	13.3	-13.0
6	5	2	8.0	8.0
7	5	-2	8.1	-6.7
0	5	3	14.3	-14.0
1	5	-3	15.1	15.6
1	5	3	12.1	-12.3
2	5	-3	15.6	15.8
2	5	3	3.3	-3.0
3	5	-3	9.6	9.2
3	5	3	3.6	2.9
4	5	-3	-1.6	-3.0
4	5	3	11.6	10.9
5	5	-3	9.5	-9.7
5	5	3	6.2	4.9
6	5	-3	-1.7	-1.7
6	5	3	-1.5	-2.5
7	5	-3	-1.8	-0.6
0	5	4	14.6	-13.3
1	5	-4	-1.4	0.8
1	5	4	2.5	-2.4
2	5	-4	22.4	-23.5
2	5	4	5.2	-5.1
3	5	-4	14.2	-13.3
3	5	4	-1.3	1.2
4	5	-4	6.7	5.5
4	5	4	10.8	10.1
5	5	-4	10.8	10.8
5	5	4	13.6	13.3
6	5	-4	5.4	5.5
7	5	-4	-1.8	-0.6
0	5	5	-1.2	1.6
1	5	-5	9.1	-9.1
1	5	5	3.2	3.9
2	5	-5	4.7	-4.2
2	5	5	9.3	10.7
3	5	-5	7.1	6.7
3	5	5	3.3	3.6
4	5	-5	6.4	5.7
4	5	5	5.0	-4.8
5	5	-5	10.9	8.0
5	5	5	-1.5	-2.3
6	5	-5	5.2	-4.7
7	5	-5	-1.8	-4.2
0	5	6	11.9	-10.9
1	5	-6	8.5	9.3
1	5	6	2.3	-2.2
2	5	-6	12.7	12.8
2	5	6	3.6	3.6
3	5	-6	-1.5	-2.0
3	5	6	-1.4	-1.1
4	5	-6	-1.6	-2.9
4	5	6	-1.4	2.1
5	5	-6	-1.6	3.0
5	5	6	3.7	-3.6
6	5	-6	4.9	5.2
7	5	-6	7.2	6.9
0	5	7	-1.3	1.8
1	5	-7	2.9	-0.6
1	5	7	4.3	5.0
2	5	-7	3.1	-2.1
2	5	7	-1.3	0.2
3	5	-7	10.3	-10.6
3	5	7	3.1	-2.6
4	5	-7	3.9	-3.7
4	5	7	-1.5	-1.5
5	5	-7	-1.6	1.4
6	5	-7	7.2	7.8
7	5	-7	-1.9	1.9
0	5	8	-1.3	2.5
1	5	-8	10.3	10.9
1	5	8	4.5	4.5
2	5	-8	3.7	2.7
2	5	8	4.3	5.5
3	5	-8	4.7	4.5
3	5	8	-1.4	-1.6
4	5	-8	7.2	7.0
4	5	8	9.4	-9.0
5	5	-8	6.9	-7.1
6	5	-8	8.8	-9.3
7	5	-8	-1.8	0.7
0	5	9	2.7	-2.5
1	5	-9	4.5	4.7
1	5	9	5.4	-5.8
2	5	-9	3.5	4.2
2	5	9	6.8	-6.6
3	5	-9	-1.6	0.6
3	5	9	-1.4	-1.7
4	5	-9	-1.5	-2.6
5	5	-9	-1.7	-1.9
6	5	-9	-1.7	-2.9
7	5	-9	-1.8	-2.5
0	5	10	6.9	6.6
1	5	-10	8.2	-8.5
1	5	10	6.6	8.1
2	5	-10	-1.6	-2.3
2	5	10	8.1	-7.6
3	5	-10	7.7	8.2
3	5	10	7.6	-7.3
4	5	-10	-1.6	3.0
5	5	-10	-1.7	2.5
6	5	-10	-1.8	-4.2
7	5	-10	8.1	-8.0
0	5	11	10.9	-9.6
1	5	-11	-1.6	1.4
1	5	11	8.2	-7.6
2	5	-11	8.6	9.7
2	5	11	-1.5	0.1
3	5	-11	11.4	11.5
4	5	-11	-1.7	1.6
5	5	-11	6.6	-7.0
6	5	-11	6.9	-6.3
0	5	12	8.7	-7.2
1	5	-12	6.1	-6.8
1	5	12	13.5	-14.3
2	5	-12	7.7	-8.1
2	5	12	-1.5	-1.4
3	5	-12	9.5	-9.8
4	5	-12	3.1	1.7
5	5	-12	5.5	5.9
6	5	-12	7.3	6.9
0	5	13	5.5	5.2
1	5	-13	-1.7	-2.7
1	5	13	-1.5	1.8
2	5	-13	-1.7	-0.6
3	5	-13	-1.7	-0.3
4	5	-13	-1.7	-0.5
5	5	-13	-1.8	3.2
6	5	-13	-1.8	-0.8
0	5	14	-1.5	-1.0
1	5	-14	12.0	12.4
2	5	-14	4.2	4.3
3	5	-14	4.5	-3.9
4	5	-14	9.1	-9.0
5	5	-14	6.5	-6.1
1	5	-15	4.0	2.7
2	5	-15	-1.8	1.2
3	5	-15	6.2	-6.6
4	5	-15	-1.8	-3.8
5	5	-15	4.1	-2.7
0	6	0	30.7	29.2
1	6	0	10.5	7.3
2	6	0	6.5	-6.9
3	6	0	8.3	-7.3
4	6	0	5.0	-5.4
5	6	0	-1.8	3.7
0	6	1	9.7	-9.1
1	6	-1	5.6	4.4
1	6	1	12.5	-12.1
2	6	-1	-1.6	-1.9
2	6	1	4.6	4.3
3	6	-1	-1.7	-0.7
3	6	1	5.1	5.9
4	6	-1	-1.7	3.4
4	6	1	-1.8	-1.0
5	6	-1	-1.8	2.2
0	6	2	8.3	-4.2
1	6	-2	9.3	7.9
1	6	2	-1.4	-2.4
2	6	-2	13.5	13.4
2	6	2	9.9	-9.7
3	6	-2	-1.7	0.3
3	6	2	-1.4	2.6
4	6	-2	4.2	-3.7
4	6	2	8.1	8.4
5	6	-2	10.1	-9.1
0	6	3	-1.4	0.5
1	6	-3	3.3	-0.3
1	6	3	-1.4	-2.8
2	6	-3	5.0	3.6
2	6	3	6.9	-6.7
3	6	-3	8.1	6.4
3	6	3	-1.4	-2.8
4	6	-3	-1.7	-2.3
4	6	3	-1.5	-3.2
5	6	-3	-1.8	1.5
0	6	4	11.1	-9.5
1	6	-4	11.9	-11.4
1	6	4	4.1	-4.4
2	6	-4	10.3	-9.1
2	6	4	5.0	5.5
3	6	-4	11.3	10.3
3	6	4	3.5	3.2
4	6	-4	8.1	8.8
4	6	4	4.8	5.0
5	6	-4	-1.8	-1.7
0	6	5	6.9	-0.2
1	6	-5	9.2	-9.7
1	6	5	4.6	-5.1
2	6	-5	6.3	-6.5
2	6	5	-1.4	-0.9
3	6	-5	7.1	-6.3
3	6	5	-1.5	1.5
4	6	-5	-1.7	-0.8
5	6	-5	-1.8	-0.1
0	6	6	5.1	4.2
1	6	-6	10.1	-10.4
1	6	6	5.9	5.6
2	6	-6	10.9	-9.7
2	6	6	-1.4	1.9
3	6	-6	7.7	-6.3
3	6	6	-1.5	0.3
4	6	-6	-1.7	0.4
5	6	-6	6.1	5.8
0	6	7	7.6	7.0
1	6	-7	4.0	-4.1
1	6	7	2.9	3.3
2	6	-7	3.1	1.7
2	6	7	-1.5	1.2
3	6	-7	4.9	6.0
4	6	-7	-1.8	1.3
5	6	-7	-1.8	-3.7
0	6	8	8.3	7.7
1	6	-8	7.1	7.6
1	6	8	4.2	4.7
2	6	-8	3.8	3.8
2	6	8	7.0	-7.6
3	6	-8	4.5	-4.4
4	6	-8	9.4	-7.4
5	6	-8	6.2	-5.2
0	6	9	-1.5	1.5
1	6	-9	3.1	-3.1
1	6	9	-1.5	-2.4
2	6	-9	-1.7	1.5
3	6	-9	7.0	5.5
4	6	-9	4.0	4.5
5	6	-9	6.5	5.2
0	6	10	-1.5	-2.5
1	6	-10	4.8	5.0
2	6	-10	6.6	6.9
3	6	-10	6.1	5.7
4	6	-10	3.3	2.2
1	6	-11	-1.8	1.9
2	6	-11	-1.8	-0.8
3	6	-11	-1.8	-2.0
4	6	-11	-1.8	-2.0
2	6	-12	-1.6	-2.6
1	7	0	5.5	-3.7
0	7	1	4.5	2.4
1	7	-1	-1.8	2.2
1	7	1	-1.5	0.4
0	7	2	-1.5	-3.0
1	7	-2	-1.8	1.8
1	7	2	-1.5	-1.4
0	7	3	-1.5	-4.1
1	7	-3	-1.8	-0.0
1	7	-4	9.1	8.3

Results and Discussion

The equations of the mean plane of the individual rings as well as the equation of the mean molecular plane are given in Table 3. The individual five- and six-membered rings are strictly planar, but the molecule as a whole shows a small deviation from exact planarity. The outer atoms of the six-membered rings are displaced from the mean molecular plane (plane 1, Table 3) in the opposite direction to the atoms of the five-membered ring, so that the molecule is folded very slightly. The dihedral angles between the five-membered ring and the six-membered rings are 0.4° and 1.2°. Similar deviations from planarity were reported for dibenzoselenophene (8).

The bond lengths and valency angles are listed in Table 4 together with the corresponding bonds and angles of dibenzoselenophene (8) and carbazole (7). The distances and angles are very similar except, of course, those involving unlike atoms. There are small variations in the bond lengths in the six-membered rings, C(10)-C(11) being the longest, and C(1)-C(2) and C(3)-C(4) the shortest. These variations agree with bond order differences calculated by simple molecular orbital theory (11). The internal angles of the six-membered rings deviate slightly from 120° with angles at C(1) and C(11) being reduced to about 118° while the other angles are slightly increased. The angles in the five-membered rings of the three molecules show greater differences as a result of the difference in angle at the hetero-atom, the angles being 91.5°, 86.6°, and 108.3° for dibenzothiophene, dibenzoselenophene, and carbazole respectively. The C-S bond distance in dibenzothiophene, 1.740 (σ = 0.008)Å is close to the mean value of 1.72 Å

Table 3

Displacements ($\overset{\circ}{A}$) from mean planes (values underlined refer to the

atoms used to define the planes)

	1	2	3	4
C(1)	+0.016	+0.007	+0.015	+0.082
C(2)	+0.001	-0.011	+0.006	+0.069
C(3)	+0.009	+0.005	+0.025	+0.063
C(4)	-0.004	+0.005	+0.017	+0.033
C(5)	-0.007	+0.027	+0.022	-0.009
C(6)	+0.028	+0.074	+0.059	+0.011
C(7)	+0.012	+0.058	+0.036	-0.001
C(8)	-0.010	+0.026	+0.003	-0.006
S(9)	+0.001	+0.011	+0.001	+0.043
C(10)	-0.003	0	+0.001	+0.045
C(11)	-0.019	-0.007	-0.003	+0.014
C(12)	-0.015	+0.009	+0.004	+0.001
C(13)	-0.014	+0.011	-0.003	+0.004

Equations of planes (X', Y, Z' in $\overset{\circ}{A}$ referred to a, b, c*)

1   $-0.7534\ X' - 0.4711\ Y + 0.4587\ Z' = 0.3631$

2   $-0.7504\ X' - 0.4682\ Y + 0.4666\ Z' = 0.3751$

3   $-0.7551\ X' - 0.4647\ Y + 0.4626\ Z' = 0.3791$

4   $-0.7567\ X' - 0.4773\ Y + 0.4468\ Z' = 0.2862$

Angles between plane normals (degrees)

	2	3	4
1	0.5	0.4	0.8
2		0.4	1.3
3			1.2

Table 4

Bond distances (Å) and angles (degrees) in dibenzothiophene and related

molecules

Dibenzothiophene

σ(C-S) = 0.008 Å σ(C-S-C) = 0.4°
σ(C-C) = 0.011 σ(S-C-C) = 0.6
                               σ(C-C-C) = 0.7
σ(C-H) $\sim$ 0.1 σ(C-C-H) $\sim$ 6

	Dibenzothiophene X=S		Dibenzoselenophene[8] X=Se	Carbazole[7] X=NH
C(1)-C(2)	1.396	1.384	1.371	1.390
C(7)-C(8)	1.371			
C(2)-C(3)	1.390	1.385	1.377	1.398
C(6)-C(7)	1.380			
C(3)-C(4)	1.361	1.370	1.380	1.395
C(5)-C(6)	1.379			
C(4)-C(11)	1.391	1.392	1.395	1.400
C(5)-C(12)	1.393			
C(10)-C(11)	1.408	1.409	1.398	1.404
C(12)-C(13)	1.409			
C(1)-C(10)	1.384	1.386	1.395	1.395
C(8)-C(13)	1.387			
C(11)-C(12)	1.441	1.441	1.453	1.467
C(10)-X(9)	1.734	1.740	1.899	1.414
C(13)-X(9)	1.746			
C(1)-C(2)-C(3)	121.1	121.6	121.1	121.3
C(6)-C(7)-C(8)	122.0			
C(2)-C(3)-C(4)	121.1	120.5	120.6	120.4
C(5)-C(6)-C(7)	119.8			
C(3)-C(4)-C(11)	119.5	120.0	120.3	119.5
C(12)-C(5)-C(6)	120.4			
C(4)-C(11)-C(10)	119.2	118.7	118.1	118.8
C(5)-C(12)-C(13)	118.1			

Table 4 (Continued)

	X=S		X=Se	X=NH
C(11)-C(10)-C(1)	121.6	121.6	121.6	122.3
C(8)-C(13)-C(12)	121.5			
C(10)-C(1)-C(2)	117.4	117.8	118.7	117.7
C(7)-C(8)-C(13)	118.1			
C(11)-C(10)-S(9)	112.8	112.3	112.4	108.8
C(12)-C(13)-S(9)	111.8			
C(10)-C(11)-C(12)	111.4	111.9	114.3	107.1
C(11)-C(12)-C(13)	112.4			
C(4)-C(11)-C(12)	129.3	129.4	127.6	134.1
C(11)-C(12)-C(5)	129.4			
C(1)-C(10)-X(9)	125.6	126.2	126.0	128.9
C(8)-C(13)-X(9)	126.7			
C(10)-X(9)-C(13)	91.5	91.5	86.6	108.3

Dibenzothiophene

C(1)-H	1.09		H-C(1)-C(2,10)	114,128
C(2)-H	1.06		H-C(2)-C(1,3)	112,126
C(3)-H	0.99		H-C(3)-C(2,4)	120,117
C(4)-H	0.99		H-C(4)-C(3,11)	117,122
C(5)-H	0.90		H-C(5)-C(6,12)	126,114
C(6)-H	0.85		H-C(6)-C(5,7)	104,135
C(7)-H	0.98		H-C(7)-C(6,8)	118,120
C(8)-H	0.95		H-C(8)-C(7,13)	126,114

found for related conjugated heterocyclic molecules (12).

The hydrogen atoms have been located with less precision. The C-H bond lengths range between 0.85 and 1.09 ($\sigma = 0.12$) $\overset{\circ}{A}$ with a mean value of 0.97 $\overset{\circ}{A}$. The H-C-C valency angles vary from 104 to 135 ($\sigma = 6$)$\overset{\circ}{}$ with a mean value of 120°.

The packing of molecules in the unit cell is shown in Figure 3. The shortest heavy-atom intermolecular distance is a C(5)...C(11) distance of 3.57 $\overset{\circ}{A}$. Since only C(5) carries a hydrogen atom, there is no steric interaction. The shortest hydrogen-hydrogen intermolecular distance is 2.39 $\overset{\circ}{A}$ and involves the hydrogens of C(2) and C(7). Since the van der Waal radius of hydrogen in 1.2 $\overset{\circ}{A}$, there is no steric strain.

O   a   2a

C

4Å
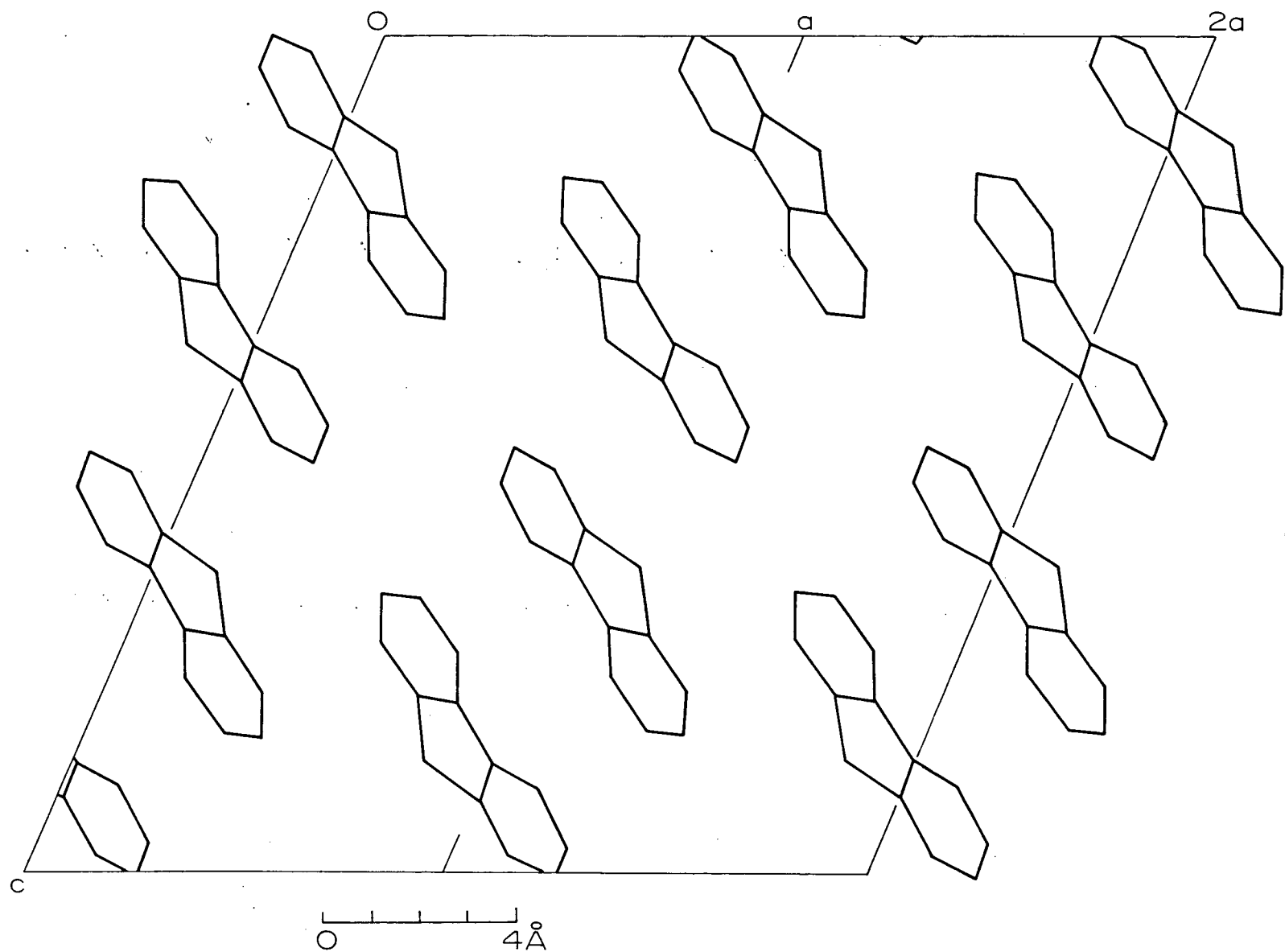
Figure 3.   Projection of the structure along b.

PART II

THE DETERMINATION OF THE STRUCTURE OF

DL-ORNITHINE HYDROBROMIDE

A. INTRODUCTION

L-ornithine $H_2N(CH_2)_3CH(NH_2)COOH$ is the key amino acid of the Krebs-Henseleit, or ornithine cycle in the mammalian liver. The highly toxic ammonia produced by the deamination of amino acids is converted into the much less toxic urea by means of the ornithine cycle. Urea, the chief nitrogen end product in mammals, is then eliminated via the kidneys. Thus, although ornithine is not a constituent amino acid of proteins, it is one of the more important amino acids in protein metabolism.

B. THE STRUCTURE OF DL-ORNITHINE HYDROBROMIDE

Experimental

DL-ornithine hydrobromide was recrystallized from water and a small single crystal was cut from a large crystalline mass. The crystal appeared to be stable at room temperature. Unit cell and space group data were determined from rotation, Weissenberg, and precession photographs.

Crystal data (λ, Cu-K_α = 1.5418 Å, λ, Mo-K_α = 0.7107 Å).

DL-ornithine hydrobromide, $C_5H_{13}N_2O_2Br$; M = 213.1; m.p. 223°.

Monoclinic, a = 12.18 $\pm$ 0.02, b = 7.88 $\pm$ 0.02, c = 11.61 $\pm$ 0.02 Å,

β = 133° 39' $\pm$ 20'.

U = 806.3 Å^3, D_m = 1.74 (floatation), Z = 4, D_x = 1.75.

F(000) = 432.

Absorption coefficient for X-rays, μ(Cu-K_α) = 72 cm^{-1}, μ(Mo-K_α) = 53 cm^{-1}.

Absent reflexions: h0ℓ when ℓ is odd, 0k0 when k is odd.

Space group is $P2_1/c$ (C_{2h}^5).

The intensities of the reflexions were estimated visually from Cu-K$_\alpha$ equi-inclination Weissenberg films of the h0ℓ-h7ℓ layers; the layers were correlated with intensities measured from Mo-K$_\alpha$ precession films of the hk0 and hkh zones. The crystal used measured 0.25 x 0.38 x 0.50 mm and was approximately a right-angled parallelepiped. Of the possible 2171 independent reflexions within the copper sphere, 1559 were observed. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Structure amplitudes were derived as usual.

Structure Analysis

The bromide ion was located by means of a three-dimensional Patterson function (0.0458, 0.1271, 0.1875). Structure factors were calculated for all the three-dimensional data for bromine alone. The scattering factor for Br$^-$ was obtained from the curve for the uncharged bromine atom from the International Tables for X-ray Crystallography (10) by comparison with the differences in the values of X$^-$ and X (X = F, Cl, I) and was corrected for anomalous dispersion according to the expression

$$f(corrected) = \sqrt{(f_{Br^-} + \Delta f'_{Br})^2 + (\Delta f''_{Br})^2}$$

using the values $\Delta f'$ and $\Delta f''$ given in the International Tables. The isotropic thermal parameter, B, was taken as 4.0 Å^2. The discrepancy factor was 0.39. A three-dimensional Fourier series was summed with

phases based on the bromide ion; in this electron-density distribution, all the carbon, nitrogen, and oxygen atoms were identified. These were introduced to the structure factor calculations with scattering factors from the International Tables and B = 4.0 $\overset{\circ}{A}{}^2$. During the first least-squares refinement cycle R dropped to 0.27. A second Fourier synthesis gave well-resolved peaks for each of the ten heavy atoms.

Further refinement of the positional and isotropic thermal parameters, together with an overall scale factor proceeded by the block-diagonal least-squares method, the function minimized being $\Sigma w(|F_o|-|F_c|)^2$. As the structure factors are least accurate for the very strong reflexions which are difficult to estimate visually, the weighting scheme employed was $\sqrt{w} = 1$ for $|F_o| < F^*$ and $\sqrt{w} = F^*/|F_o|$ for $|F_o| \geqslant F^*$, where F^* was taken as 9. After four cycles of isotropic least-squares refinement, R was 0.20. At this point the intensities of a few reflexions with very marked $|F_o|-|F_c|$ differences were re-estimated visually. After an additional six cycles of isotropic refinement, R was 0.15 and the parameter shifts were small in magnitude and random in direction.

Subsequent anisotropic cycles of refinement reduced R to 0.14. At that point the thirteen hydrogen atoms of the molecule were located by means of a difference synthesis. The hydrogen atoms are moderately well-resolved with peak densities of 0.7-1.3 $e\overset{\circ}{A}{}^{-3}$. The hydrogen atoms were introduced into the structure factor calculations with scattering factors from the International Tables and B = 4.0 $\overset{\circ}{A}{}^2$. During the final three cycles of least-squares refinement, the thermal

parameters of the hydrogen atoms were refined isotropically while those of the heavier atoms were refined anisotropically. All the parameter shifts were small and nonsystematic; the largest parameter shift during the last cycle being one-third of a standard deviation for the non-hydrogen atoms and three quarters of a standard deviation for hydrogen atoms.

The final observed and calculated structure factors are listed in Table 5; R is 0.13 for the 1559 observed reflexions. The final three-dimensional Fourier synthesis is shown in Figure 4. The atoms are well resolved with peak densities of 70 $e\mathring{A}^{-3}$ for the bromide ion, 16 $e\mathring{A}^{-3}$ for oxygen atoms, 12 $e\mathring{A}^{-3}$ for nitrogen atoms, and 10 $e\mathring{A}^{-3}$ for carbon atoms. These high peak densities may be the result of high absorption. The final three-dimensional difference synthesis revealed random fluctuations in electron density distribution as great as ± 1 $e\mathring{A}^{-3}$. However, in the vicinity of the bromide ion there is a 3 $e\mathring{A}^{-3}$ peak flanked on two sides by troughs at 2 $e\mathring{A}^{-3}$ and on each of the remaining opposing sides by a peak of 1 $e\mathring{A}^{-3}$.

The final positional and thermal parameters of the non-hydrogen atoms are in Table 6. The bond lengths and valency angles are in Table 7. The positional parameters of the hydrogen atoms which have been determined with much less accuracy are listed in Table 8, together with a summary of the molecular dimensions involving hydrogen atoms.

Results and Discussion

Due to the presence of a centre of symmetry, the unit cell contains two of each of the optical isomers of ornithine hydrobromide. The standard molecule in this analysis happens to be the D-isomer. The

Table 5

Measured and calculated structure factors (Unobserved reflexions are indicated by a minus sign in front of $|F_o|$).
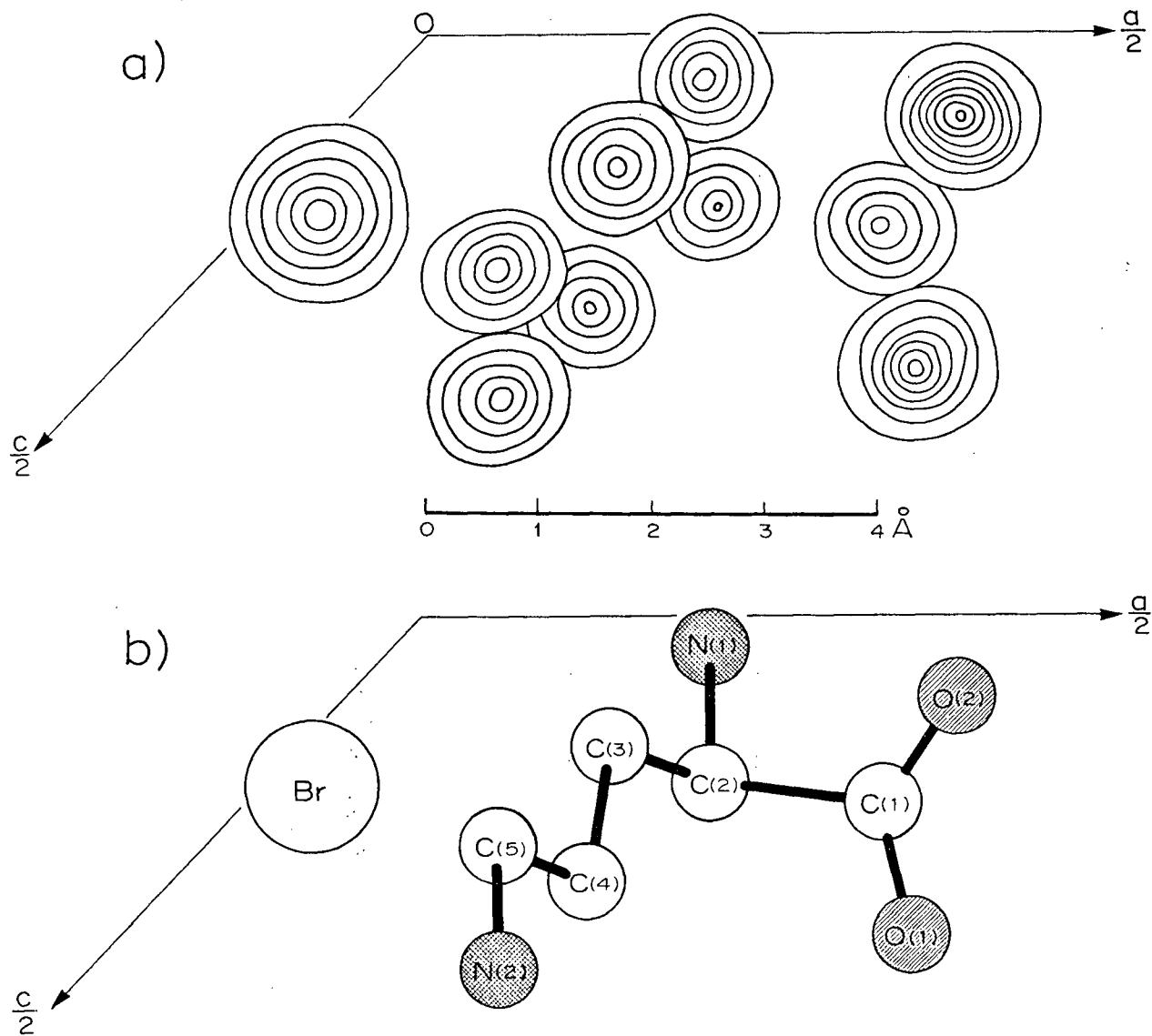
Figure 4(a). Sections of the final electron-density distribution parallel to (010). Contours at intervals of $2 \text{ e\AA}^{-3}$, except at Br where contours are at intervals of $10 \text{ e\AA}^{-3}$.

(b). A perspective drawing of the molecule as viewed along the b-axis, showing atom numbering used.

final three-dimensional electron density distribution is shown in Figure 4 together with a drawing of the molecule giving the atom numbering used in this analysis. The compound is a zwitterion, $Br^- NH_3^+ (CH_2)_3 CH(NH_3^+)COO^-$, with both nitrogens accepting protons to form tetrahedral $C-NH_3^+$ groups. The molecule is composed of two approximately planar groupings of atoms, a carboxyl group and an aliphatic side chain terminating in nitrogen atoms. The equation of the mean plane through O(1), O(2), C(1), C(2) is

$$-0.3206 \ X' + 0.9459 \ Y - 0.0501 \ Z' = 1.2152$$

where X', Y, Z' are coordinates in $\overset{o}{A}$ with reference to orthogonal axes a, b, and c*. The deviations of the atoms from the plane are: O(1), $+0.005 \ \overset{o}{A}$; O(2), $+0.005 \ \overset{o}{A}$; C(1), $-0.014 \ \overset{o}{A}$; and C(2), $+0.003 \ \overset{o}{A}$. The α-nitrogen atom, N(1), lies $0.823 \ \overset{o}{A}$ out of the plane as compared to a value of $0.436 \ \overset{o}{A}$ for L-glycine (13), $0.446 \ \overset{o}{A}$ for L-lysine hydrochloride dihydrate (14) and $0.838 \ \overset{o}{A}$ for L-ornithine hydrochloride (15). The aliphatic side-chain is fully extended; its mean plane has the equation:

$$0.8133 \ X' + 0.4790 \ Y - 0.3302 \ Z' = 2.5741$$

The deviations from the plane are N(1), $-0.074 \ \overset{o}{A}$; C(2), $+0.086 \ \overset{o}{A}$; C(3), $+0.069 \ \overset{o}{A}$; C(4), $-0.116 \ \overset{o}{A}$; C(5), $-0.029 \ \overset{o}{A}$; and N(2), $+0.050 \ \overset{o}{A}$. C(1) is displaced $+1.399 \ \overset{o}{A}$. The dihedral angle between the two planes is 77.9° as compared to 78.7° for ornithine hydrochloride (15) and 71.4° for lysine (14).

The two C-O distances are equal within experimental error, the mean value being $1.249 \ \overset{o}{A}$.

Table 6

Final positional (fractional x 10^4) and thermal ($\overset{\circ}{A}{}^2$ x 10^2) parameters,

with standard deviations in parentheses

Atom	x	y	z
C(1)	4628(15)	3446(22)	2064(16)
C(2)	3243(12)	2833(22)	1749(15)
C(3)	2284(13)	4375(23)	1371(14)
C(4)	3073(14)	5464(26)	2857(15)
C(5)	2141(13)	7068(23)	2421(14)
N(1)	2316(13)	1615(21)	0435(15)
N(2)	3032(12)	8259(22)	3772(13)
O(1)	5823(11)	3692(15)	3481(13)
O(2)	4434(11)	3710(16)	0873(12)
Br	0447(1)	1279(2)	1891(2)

Atom	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
C(1)	2.56	0.55	1.75	2.98	0.27	3.33
C(2)	2.20	-0.16	1.98	2.77	0.01	3.72
C(3)	2.37	-0.41	1.92	3.18	-0.51	3.23
C(4)	3.41	0.35	2.32	4.48	-0.47	3.36
C(5)	2.80	0.06	1.94	3.08	-0.32	2.90
N(1)	3.32	-0.06	2.31	2.90	-0.05	4.31
N(2)	2.96	-0.11	2.05	4.16	-0.58	3.36
O(1)	2.45	-0.25	2.18	4.00	0.27	4.37
O(2)	4.11	0.09	3.25	5.06	0.81	4.19
Br	3.20	-0.10	2.22	3.85	-0.09	3.66
Mean σ:						
C,N,O	0.35	0.44	0.23	0.85	0.44	0.35
Br	0.05	0.04	0.04	0.14	0.05	0.06

Table 7

Bond distances (Å) and angles (degrees) (σ = 0.02 Å and 1.5°)

C(1)-C(2)	1.537		C(1)-C(2)-C(3)	108.3
C(2)-C(3)	1.525		C(2)-C(3)-C(4)	111.2
C(3)-C(4)	1.532		C(3)-C(4)-C(5)	110.1
C(4)-C(5)	1.533		Mean C-C-C	109.9
Mean C-C	1.532			
			C(1)-C(2)-N(1)	112.6
C(2)-N(1)	1.465		C(3)-C(2)-N(1)	109.6
C(5)-N(2)	1.473		C(4)-C(5)-N(2)	109.9
Mean C-N	1.469		Mean C-C-N	110.7
C(1)-O(1)	1.249		C(2)-C(1)-O(1)	116.8
C(1)-O(2)	1.248		C(2)-C(1)-O(2)	116.9
Mean C-O	1.249		Mean C-C-O	116.9
			O(1)-C(1)-O(2)	126.2

Table 8

Hydrogen atoms

Positional parameters (fraction x 10^3; $\sigma \sim 0.25$ Å; the mean B being 1.3 Å^2), bond lengths (Å, $\sigma \sim 0.25$ Å), and valency angles (degrees, $\sigma \sim 15 - 20°$)

Atom	Bonded to	x	y	z
H(1)	N(1)	269	077	049
H(2)	N(1)	185	205	-055
H(3)	N(1)	157	098	013
H(4)	N(2)	393	832	411
H(5)	N(2)	360	762	494
H(6)	N(2)	260	903	369
H(7)	C(2)	358	250	284
H(8)	C(3)	217	517	031
H(9)	C(3)	123	398	093
H(10)	C(4)	470	563	381
H(11)	C(4)	283	493	374
H(12)	C(5)	192	752	152
H(13)	C(5)	155	725	256

N-H	0.8-1.1, mean 0.9
C-H	0.9-1.4, mean 1.1
C-N-H	107-130, mean 117
H-N-H	86-124, mean 101
C-C-H N-C-H }	78-127, mean 108
H-C-H	111-120, mean 114

Table 9

Carbon-oxygen bond lengths in some amino acids

Amino Acid	C(1)-O(1)	C(1)-O(2)	Mean
DL-ornithine hydrobromide	1.249 Å	1.248 Å	1.249 Å
L-ornithine hydrochloride	1.257	1.245	1.251
L-lysine hydrochloride dihydrate	1.250	1.246	1.248
L-alanine	1.247	1.256	1.253

As shown in Table 9, these values agree well with the corresponding internuclear distances of other amino acids. The two $C-NH_3^+$ bonds also are equal within experimental error (Table 7); the average value of 1.469 Å is similar to that of 1.482 Å for L-lysine (14), and that of 1.492 Å for ornithine hydrochloride (15), these differences probably not being significant. The C-C bond lengths do not differ significantly from each other (Table 7). The mean C-C distance of 1.532 Å agrees well with the single bond length of 1.533 proposed by Bartell (16) on the basis of electron diffraction studies of normal hydrocarbons butane through heptane. The mean C-C distance is similar to the analogous values of 1.524 Å for lysine (14), 1.525 Å for L-alanine (17), and 1.530 Å for ornithine hydrochloride (15). The bond angles of the carboxylate group are equal within the limits of experimental error to the analogous angles in lysine (14), and ornithine (15).

Table 10

Carboxylate bond angles in ornithine and lysine derivatives

Angle	Compound		
	Ornithine HBr	Ornithine HCl	Lysine HCl·$2H_2O$
O(1)-C(1)-O(2)	126.2°	126.6°	125.5°
C(2)-C(1)-O(1)	116.8	116.0	116.8
C(2)-C(1)-O(2)	116.9	117.0	117.7

Similarly, the C-C-N angles of the above compounds resemble one another; however, the agreement is not so good as in the case of the carboxylate group angles.

Table 11

Carbon-carbon-nitrogen angles in ornithine and lysine derivatives

Angle	Compound		
	Ornithine HBr	Ornithine HCl	Lysine HCl·$2H_2O$
C(1)-C(2)-N(1)	112.6°	110.3°	109.7°
C(3)-C(2)-N(1)	109.6	107.8	111.8
C(4)-C(5)-N(2)	109.9	110.4	
C(5)-C(6)-N(2)			110.9

The C-C-C angles of the three amino acids are similar and close to the tetrahedral value of 109.5.

Table 12

Carbon–carbon–carbon angles in ornithine and lysine derivatives

Angle	Compound		
	Ornithine·HBr	Ornithine·HCl	Lysine HCl·$2H_2O$
C(1)–C(2)–C(3)	108.3°	110.2°	109.8°
C(2)–C(3)–C(4)	111.2	112.4	114.6
C(3)–C(4)–C(5)	110.1	109.0	110.0
C(4)–C(5)–C(6)			111.5

The visual data are not sufficiently accurate to yield reliable values for the hydrogen parameters. The average N–H bond length of 0.89 Å is close to the value of 0.94 Å for lysine (14), and 0.95 Å for ornithine hydrochloride (15). On the other hand, all these bonds are somewhat shorter than the standard N–H bond distance of 1.03 Å for the ammonium ion and that of 1.01 Å for ammonia. However, these differences are not significant.

The mean C–H bond length of 1.14 Å is insignificantly longer than the analogous mean values of 1.06 and 1.05 Å for lysine (14) and ornithine (15) respectively.

A projection of the structure is shown in Figure 5. The most significant feature of the packing is a system of three N–H...O and three N–H...Br hydrogen bonds involving all six active hydrogen atoms. The terminal nitrogen atom, N(2), donates three protons, one to the bromide ion of the standard molecule at [010], another to the carboxylate O(2) of the nearest screw-axis-generated molecule at [111] and the last
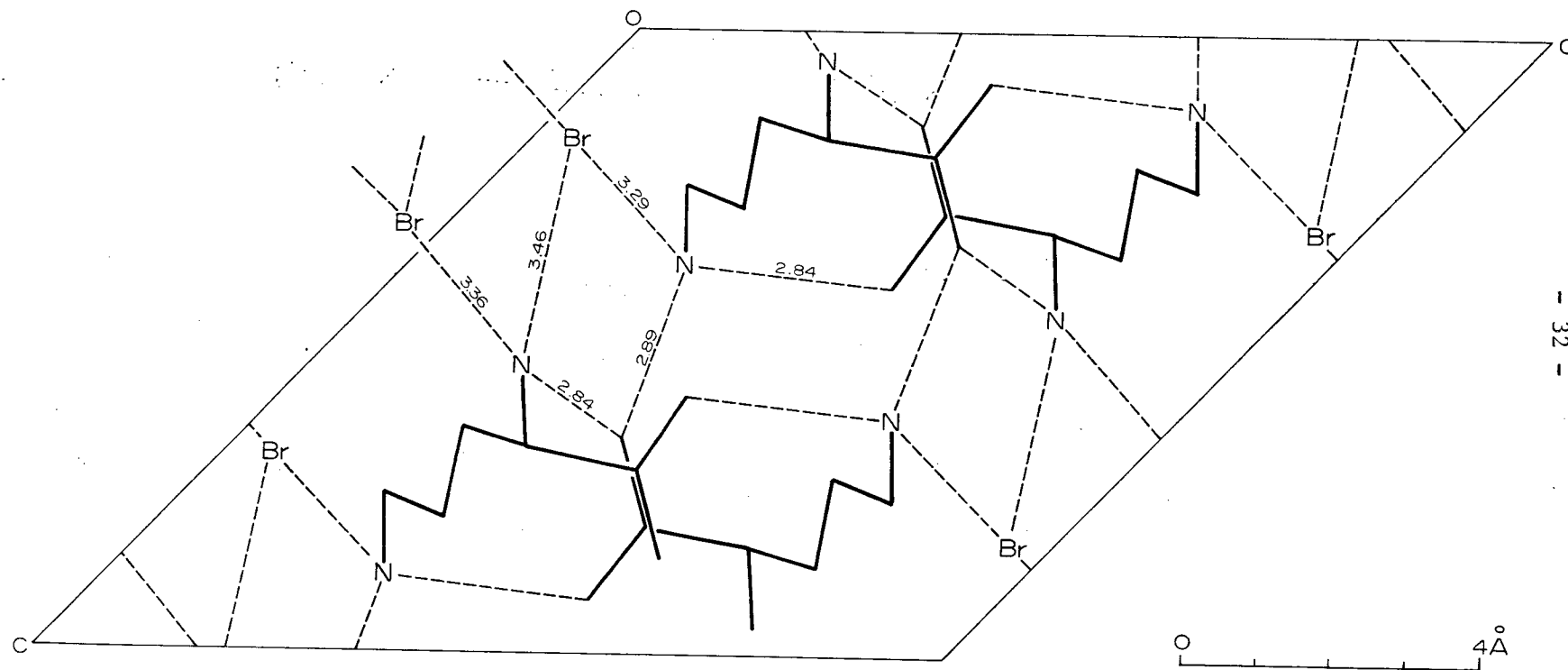
Figure 5.   Projection of the structure along b; broken lines are hydrogen bonds.

proton to the carboxylate O(1) of the adjacent center-of-symmetry-
generated molecule at [111]. The side-chain nitrogen atom, N(1),
also donates three protons, one to the carboxylate O(1) of the closest
screw-axis-generated molecule at [101] and the remainder to nearby
bromide ions. The hydrogen bond distances and angles are in Table 13.
One of the C-N...Br angles is 155°, but the other C-N...O,Br angles
are all in the range 95-109°. The positions of the hydrogen atoms
support the hydrogen bond assignments; the H...O distances are about
2.0 Å, the H...Br distances 2.6 Å, and the bonds all show the
usual deviations from exact linearity, the H-N...O, Br angles varying
from 7° to 25°. There is one further short N(2)...O(2) internuclear
contact of 2.97 Å, but the C-N...O angle is 166° and there is no
intervening hydrogen atom, the shortest H...O distance being 2.6 Å,
so that this contact does not represent a hydrogen bond. The N-H...O
distances (2.84, 2.84, 2.89 Å) and the N-H...Br distances (3.29, 3.36,
3.46 Å) are close to the values usually found in these types of systems
(18). The bromide ion acts as an acceptor for three hydrogen bonds,
the N...Br⁻...N angles being 91, 91, and 139°. O(1) accepts two
protons, the C-O...N angles being 124° and 127°, and the N...O...N
angle 108°. O(2) accepts one hydrogen bond, and the C-O...N angle is
118°. The above system of hydrogen bonds is complex in that the five
heavier atoms of the standard molecule participate in twelve hydrogen
bonds which involve the corresponding atoms [N(1), N(2), O(1), O(2), Br] in
twelve different molecules.

The structure of DL-ornithine hydrobromide is similar to that of
L-ornithine hydrochloride. Layers of L-ornithine molecules parallel

to the ab plane are almost identical in the structures. In L-ornithine

hydrochloride these layers are stacked along c, giving a c-axis of 5 $\overset{\circ}{A}$;

in DL-ornithine hydrobromide, the layers of L-ornithine molecules are

related by the c glide plane to layers of D-molecules (Figure 5)

resulting in a c-axis of about double the length.

Table 13

Distances (Å) and angles (degrees) in the hydrogen bonds, N-H...A

(A = O or Br)

Bond	N...A	C-N...A
N(1)-H(1)...O(1), IV[101]	2.84	105
N(1)-H(2)...Br, II[001]	3.46	109
N(1)-H(3)...Br, III[000]	3.36	155
N(2)-H(4)...O(2), IV[111]	2.84	99
N(2)-H(5)...O(1), III[111]	2.89	106
N(2)-H(6)...Br, I[010]	3.29	95

Equivalent positions are

I	x	y	z
II	x	$\frac{1}{2} - y$	$\frac{1}{2} + z$
III	-x	-y	-z
IV	-x	$-\frac{1}{2} + y$	$-\frac{1}{2} - z$

together with translation in a, b, and c indicated in square brackets.

PART III

THE DETERMINATION OF THE STRUCTURE OF

HISTAMINE DIPHOSPHATE MONOHYDRATE

A. INTRODUCTION

Histamine, one of the most important autacoids in the human body, is synthesized in vivo by the enzymatic decarboxylation of histidine. Almost all mammalian tissues contain histamine and are capable of synthesizing it. The histamine which is released by injured body tissues gives rise to many of the signs and symptoms of trauma and allergy.

B. THE STRUCTURE OF HISTAMINE DIPHOSPHATE MONOHYDRATE

Experimental

Histamine diphosphate was recrystallized from water. The resultant colorless, transparent, needle-shaped crystals are elongated along a and appear to be stable in room air; no radiation damage was observed. The unit cell parameters and space group were determined from various rotation, Weissenberg and precession films. The melting point could not be determined as the crystal began to lose water of hydration at 88° and became completely liquid at 118°C.

Crystal data (λ, Mo-K_α = 0.7107 $\overset{\circ}{A}$).

4-(2-aminoethyl)-imidazole diphosphate monohydrate, $C_5H_{17}N_3O_9P_2$;

  M = 325.2.

Monoclinic, a = 7.99 $\pm$ 0.01, b = 13.17 $\pm$ 0.01, c = 13.19 $\pm$ 0.01 $\overset{\circ}{A}$,

  β = 111.2 $\pm$ 0.1°.

U = 1294 $\overset{\circ}{A}{}^3$, D_m = 1.669 (floatation), Z = 4, D_x = 1.668.

F(000) = 680

Absorption coefficient for X-rays, μ(Mo-K_α) = 3.90 cm^{-1}.

Absent reflexions: h0ℓ when ℓ is odd, 0k0 when k is odd.

Space group P2$_1$/c (C_{2h}^5).

The intensities of all reflexions with 2θ(Mo-K_α) less than 46°

were measured on a G.E. XRD-5 Spectrogoniometer, with Single Crystal

Orienter, using a scintillation counter, Mo-K$_\alpha$ radiation (zirconium

filter and pulse height analyzer), and the moving-crystal moving-

counter technique (9). The corresponding minimum interplanar spacing

is 0.91 Å. All the intensities were corrected for background and

the structure amplitudes were derived as usual. The crystal,

measuring 0.5 x 0.5 x 2.0 mm, was mounted with a*

parallel to the goniostat axis. Possible errors in the measured

structure factors were examined. Considering the crystal as a cylinder

of mean diameter 0.5 mm, μR is 0.0975 and hence the absorption correc-

tion factor A* is 1.10 and constant in the range θ = 0-40°; therefore,

the error due to absorption is negligible. In addition, absorption

errors due to non-uniformity of crystal dimension were estimated by

considering the longest and shortest path lengths in the cross-section

of the crystal. The absorption corrections for the corresponding

structure factors are exp (3.9 x 0.07/2) and exp (3.9 x 0.05/2), that

is 1.15 and 1.10 respectively. Thus the maximum deviation from the

mean correction of 1.125 is 0.025 or 2.2%. Since the cumulative possible

maximum error in F$_o$ due to absorption is less than 2.3% and since the

majority of errors will be much smaller than this value, no correction

was made for absorption. 1747 reflexions in the range 0 < 2θ < 46° were

observed; 1554 (89%) had intensities above background.

Structure Analysis

The positions of the two phosphorus atoms were determined from a

three-dimensional Patterson synthesis (P-1, 0.333, 0.125, 0.370; P-2,

0.740, 0.290, 0.216) and structure factors were calculated for all the

three-dimensional data for phosphorus only using scattering factors

from the International Tables for X-ray Crystallography, 1962 (10)

and isotropic thermal parameters of 4.0 $\overset{\circ}{A}^2$. The discrepancy factor, R,

was 0.57 for the observed reflexions. A three-dimensional Fourier

synthesis with the phase angles based on the phosphorus atoms revealed

the positions of all the non-hydrogen atoms. When these were introduced

into the structure factor calculations with scattering factors from the

International Tables and B = 4.0 $\overset{\circ}{A}^2$, R dropped to 0.32. Subsequent

refinement of the positional and isotropic thermal parameters together

with an overall scale factor, was carried out by means of the block-

diagonal least-squares method, the function minimized being

$\Sigma w(|F_o| - |F_c|)^2$. Since the structure factors were considered to be

least accurately measured for the strong reflexions which are most

affected by absorption as well as for the weak reflexions whose

intensities are similar to that of background radiation, the following

weighting scheme was employed:

$$\sqrt{w} = \frac{1}{\sqrt{1 + \left(\dfrac{|F_o| - F^*}{G^*}\right)^2}}$$

where $F^* = 16$ and $G^* = 26$. This scheme gives $\sqrt{w} = 0.80$ for $|F_o| = 1$,

maximum $\sqrt{w} = 1$ for $|F_o| = 16$ and thereafter decreasing weights so that

at $|F_o| = 42$, for example, $\sqrt{w} = 0.71$. Unobserved reflexions were

assigned $\sqrt{w} = 0.29$.

After seven isotropic least-squares refinement cycles, R was 0.12; shifts

in positional parameters were about one-third of a standard deviation while

thermal parameter shifts were of the order of one standard deviation.
The parameter shifts of the water oxygen atom, however, were larger.
Therefore, its position was redetermined on an additional difference
synthesis.

Six anisotropic refinement cycles reduced R to 0.09. Thereafter,
a difference synthesis was summed and all 17 hydrogen atoms (with peak
values of 0.5-0.7 e$\overset{\circ}{A}^{-3}$) were located (Figure 6). The hydrogen atoms
were included in subsequent structure factor calculations with
scattering factors from the International Tables and B = 4.0 $\overset{\circ}{A}^2$. After
six refinement cycles in which the thermal parameters of the heavy
atoms were refined anisotropically while those of the hydrogens were
refined isotropically, R was 0.07. However, as the temperature factors
of the water hydrogens were too high at this point, their positions
were redetermined on a difference synthesis. At the completion of the
final series of eight least-squares refinements, the positional
parameter shifts were small and nonsystematic, the largest shift being
one-sixth of a standard deviation for the heavy atoms and one-third
of a standard deviation for the hydrogen atoms.

The positional and anisotropic thermal parameters of the heavier
atoms from the final least-squares cycle are given in Table 14, together
with their standard deviations computed from the inverses of the diagonal
terms of the matrix of the least-squares normal equations. Also
listed in Table 14 are the hydrogen atom positional and isotropic thermal
parameters together with their standard deviations. The final electron-
density distribution is shown in Figure 7, the atom numbering used in
Figure 8.
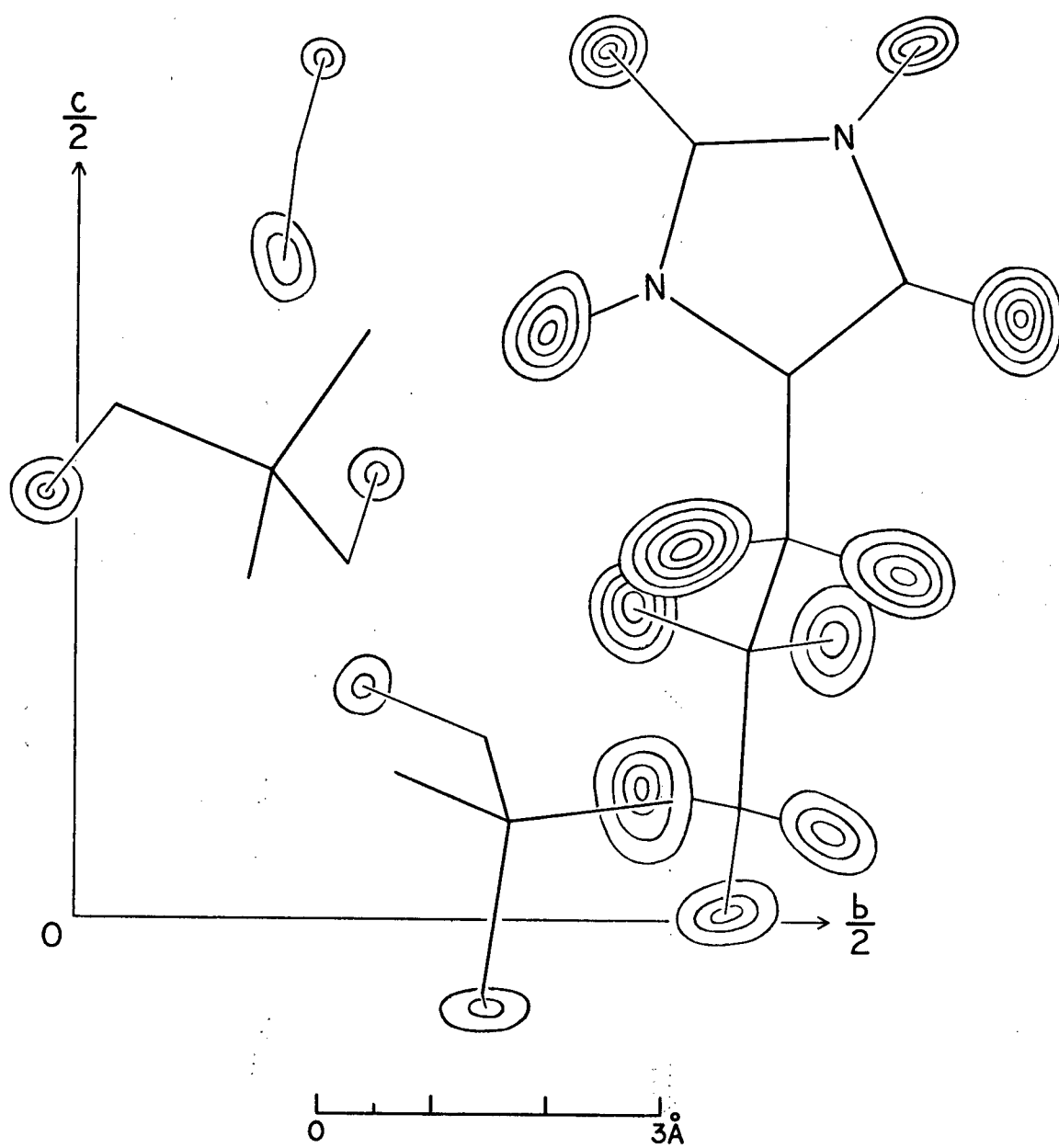
Figure 6. Difference synthesis viewed along a[*] showing the hydrogen atoms; contours at 0.4, 0.5, 0.6, 0.7, 0.8 eÅ^{-3}.

Table 14

Final positional parameters (fractional, x 10^4 for P, O, N, and C; x 10^3 for H) and thermal parameters (U_{ij} in $\overset{\circ}{A}{}^2$ x 10^2; B in $\overset{\circ}{A}{}^2$), with their standard deviations in parentheses [σ(B) for hydrogen=3-4 $\overset{\circ}{A}{}^2$].

Atom	x	y	z	B
P(1)	3466(4)	1287(2)	3749(2)	
P(2)	7489(4)	2879(2)	2299(2)	
O(3)	1917(11)	1800(7)	2789(6)	
O(4)	2743(11)	0259(7)	4005(6)	
O(5)	3879(11)	1925(7)	4759(6)	
O(6)	4989(11)	1139(7)	3351(7)	
O(7)	5669(11)	2715(7)	2463(7)	
O(8)	7098(11)	2715(7)	1062(7)	
O(9)	8026(12)	3965(7)	2565(7)	
O(10)	8852(11)	2118(7)	2915(7)	
N(11)	2734(14)	4402(9)	1352(8)	
C(12)	1971(17)	4447(12)	2232(10)	
C(13)	3389(19)	4695(12)	3299(11)	
C(14)	2775(16)	4695(10)	4246(10)	
C(15)	2361(17)	5467(10)	4782(10)	
N(16)	2046(14)	5058(8)	5662(8)	
C(17)	2231(16)	4070(10)	5648(9)	
N(18)	2659(14)	3819(8)	4790(8)	
O(w,19)	9536(15)	1440(13)	4990(9)	
H(20)	363(23)	379(13)	166(13)	3.8
H(21)	187(17)	433(10)	065(10)	1.3
H(22)	323(22)	504(13)	121(13)	3.7
H(23)	117(18)	375(11)	226(11)	1.5
H(24)	099(18)	500(11)	208(11)	1.7
H(25)	424(17)	407(11)	338(10)	1.3
H(26)	394(19)	540(11)	319(11)	2.3
H(27)	234(13)	624(8)	461(8)	1.0
H(28)	204(18)	542(11)	628(11)	2.0
H(29)	196(13)	355(8)	615(8)	1.0
H(30)	295(18)	315(11)	469(11)	1.7
H(31)	894(25)	167(15)	430(15)	5.5
H(32)	870(25)	160(15)	540(15)	5.5
H(33)	084(22)	192(13)	296(13)	3.7
H(34)	561(22)	212(13)	283(13)	3.7
H(35)	612(21)	278(13)	076(13)	3.2
H(36)	753(24)	485(14)	151(14)	4.7

Table 14 (Continued)

Atom	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
P(1)	2.53(12)	0.06(12)	1.43(9)	2.69(16)	-0.06(12)	2.80(12)
P(2)	2.78(13)	0.64(12)	1.43(10)	2.43(15)	0.43(12)	3.10(13)
O(3)	3.36(38)	1.17(40)	1.50(28)	5.57(55)	0.64(39)	2.87(36)
O(4)	4.55(40)	-1.11(39)	2.22(29)	3.61(47)	-0.36(37)	3.62(37)
O(5)	3.53(40)	0.20(37)	1.31(30)	3.50(46)	-0.91(37)	3.49(38)
O(6)	3.38(37)	0.39(36)	2.08(29)	3.45(47)	0.40(38)	4.40(40)
O(7)	4.56(40)	1.72(41)	3.54(32)	4.78(54)	2.18(44)	6.57(47)
O(8)	3.39(40)	0.55(38)	1.19(31)	4.05(48)	-0.76(39)	3.59(40)
O(9)	6.24(51)	0.05(42)	2.07(35)	3.07(47)	0.05(39)	3.78(41)
O(10)	3.45(40)	0.62(40)	1.58(31)	4.43(51)	1.21(41)	4.16(41)
N(11)	4.74(53)	-0.18(51)	2.26(37)	4.47(65)	-0.60(48)	3.63(47)
C(12)	3.77(62)	0.12(62)	1.48(45)	5.43(84)	0.26(61)	3.26(57)
C(13)	4.64(64)	-0.47(67)	2.09(46)	5.63(87)	0.39(65)	3.95(60)
C(14)	3.13(56)	-0.15(55)	1.39(43)	4.03(72)	0.36(56)	3.48(57)
C(15)	3.91(58)	-0.09(55)	1.68(44)	3.34(67)	0.22(55)	3.66(57)
N(16)	4.25(51)	0.19(47)	1.61(36)	3.62(58)	-0.37(44)	2.99(45)
C(17)	3.55(57)	0.20(54)	1.28(42)	3.62(67)	1.09(52)	2.78(51)
N(18)	4.60(54)	0.02(47)	1.86(40)	2.78(54)	-0.36(46)	4.05(51)
O(19)	7.66(60)	7.99(69)	4.36(45)	18.55(121)	6.73(70)	7.02(58)
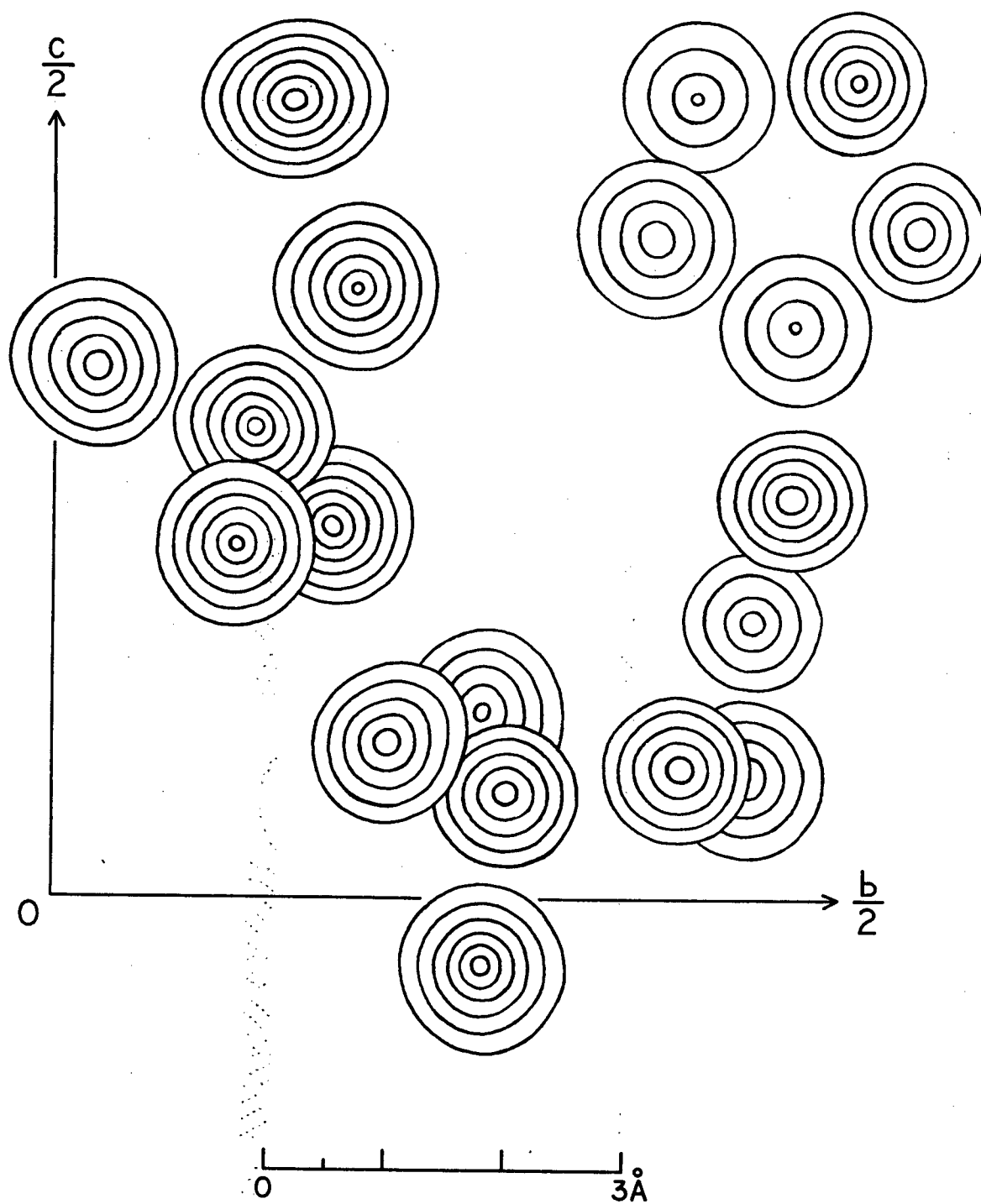
Figure 7. Electron-density distribution viewed along a^*; contours at 5, 10, 15...$e\text{Å}^{-3}$ for P, and at 2, 4, 6...$e\text{Å}^{-3}$ for C, N, and O.
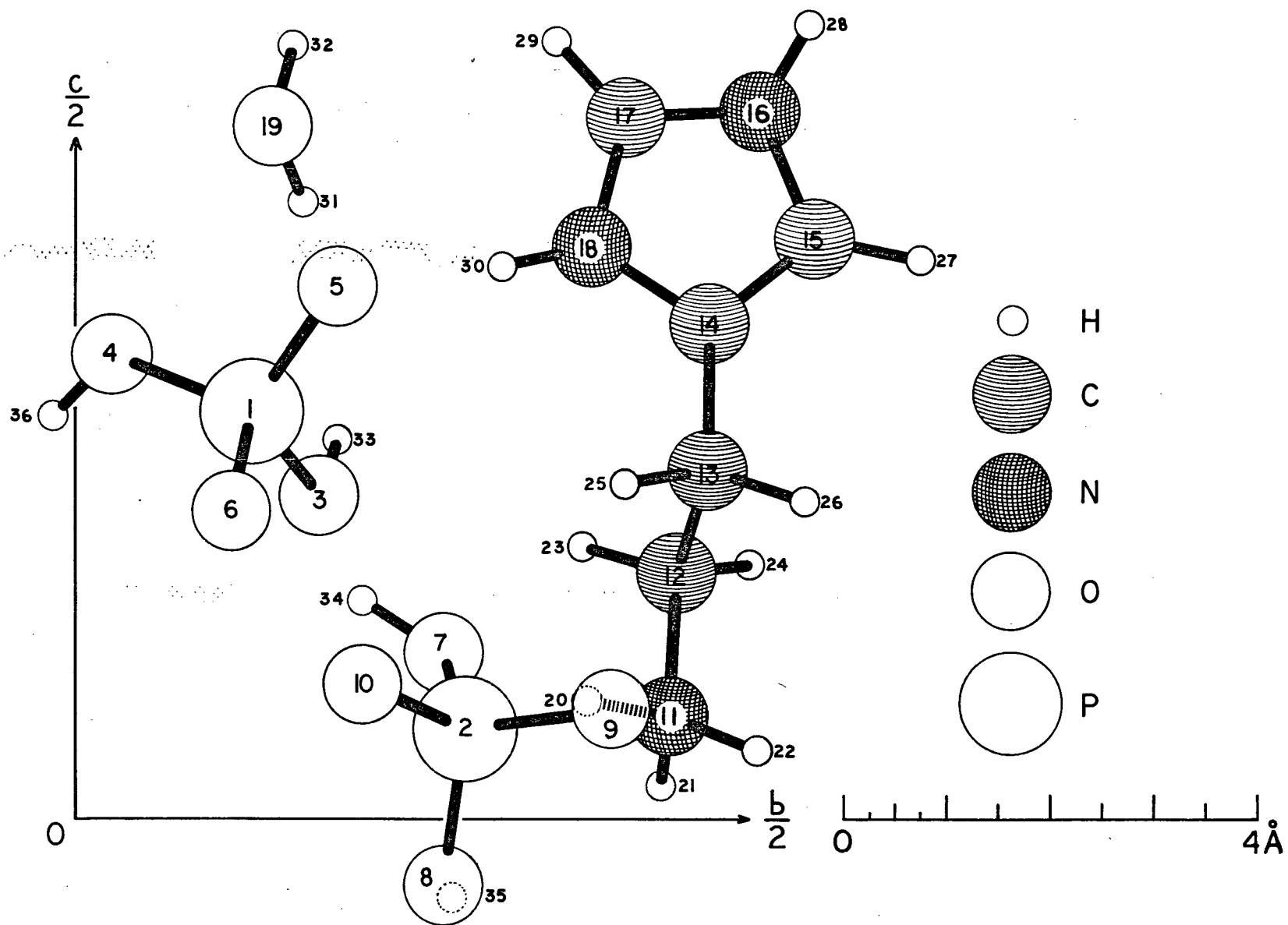
Figure 8. Drawing of the structure viewed along a* and showing the atom numbering used.

The final measured and calculated structure factors are given in Table 15; R is 0.072 for 1554 independent observed reflexions. A final three-dimensional difference synthesis was computed and showed random fluctuations as high as ± 0.6 e$\overset{\circ}{A}^{-3}$.

Results and Discussion

The structure contains a histamine cation, two $H_2PO_4^-$ anions and a molecule of water. The imidazole ring of histamine appears to be planar within the limits of experimental error. The equation of the mean plane is

$$0.8206 \; X' + 0.0908 \; Y + 0.5642 \; Z' = 3.659$$

where X', Y, and Z' are coordinates in $\overset{\circ}{A}$ referred to the orthogonal axes a, b, and c*. The deviations of the atoms from the mean plane are: C(14), +0.009 $\overset{\circ}{A}$; C(15), -0.008 $\overset{\circ}{A}$; N(16), +0.004 $\overset{\circ}{A}$; C(17), +0.002 $\overset{\circ}{A}$; and N(18), -0.007 $\overset{\circ}{A}$. The deviations of the corresponding hydrogen atoms from the plane of the imidazole ring are: H(27), +0.02 $\overset{\circ}{A}$; H(28), +0.23 $\overset{\circ}{A}$; H(29), -0.08 $\overset{\circ}{A}$; and H(30), +0.08 $\overset{\circ}{A}$. Thus the hydrogens lie in the plane of the heterocyclic ring within the limits of accuracy of the method. The deviations of the side chain atoms from the imidazole plane are: C(13), +0.12 $\overset{\circ}{A}$; C(12), -1.16 $\overset{\circ}{A}$; and N(11), -0.93 $\overset{\circ}{A}$; all highly significant displacements. The ethylamine side chain is approximately planar; the equation of the mean plane through N(11), C(12), C(13), C(14) being:

$$-0.1541 \; X' + 0.9743 \; Y - 0.1643 \; Z' = 5.159$$

with deviations of +0.021, -0.018, -0.024, and +0.021 $\overset{\circ}{A}$ respectively. The dihedral angle between the plane of the ring and the plane of the side chain is 82.5°. However, the plane of the chain does not bisect the ring, instead it is rotated toward N(18) so that

Table 15

Measured and calculated structure factors (Unobserved reflexions are indicated by a negative sign in front of $|F_o|$).

k l	/Fo/	Fc

h=0

0	2	58.2	-53.9
0	4	67.6	62.8
0	6	50.3	-47.9
0	8	62.3	63.1
0	10	-2.0	-2.9
0	12	-2.3	-7.2
1	1	17.9	-11.7
1	3	96.2	95.8
1	5	6.1	6.0
1	7	26.5	-26.6
1	9	45.2	-48.4
1	11	16.3	17.2
1	13	-2.4	6.6
2	0	13.3	-9.
2	2	92.8	89.8
2	4	92.5	-92.3
2	6	16.1	17.5
2	8	30.9	-33.7
2	10	5.6	-7.0
2	12	10.8	11.4
3	1	111.1	105.1
3	3	39.0	-26.8
3	5	45.0	45.5
3	7	10.8	-10.7
3	9	20.1	21.4
3	11	17.3	-17.6
3	13	10.2	9.3
4	0	16.3	15.4
4	2	32.3	-32.5
4	4	-1.4	11.0
4	6	53.4	-55.5
4	8	32.6	-28.9
4	10	10.5	9.
4	12	13.1	10.4
5	1	28.8	-26.7
5	3	24.6	-20.8
5	5	48.3	-48.1
5	7	44.7	46.7
5	9	38.1	-40.8
5	11	11.8	12.6
6	0	10.7	-8.4
6	2	39.9	38.2
6	4	-1.6	-4.0
6	6	-1.8	9.0
6	8	8.6	-7.9
6	10	9.8	16.0
6	12	-2.4	-0.9
7	1	13.2	12.6
7	3	5.2	-5.9
7	5	31.3	32.7
7	7	44.5	-42.7
7	9	10.7	11.3
7	11	13.4	-13.6
8	0	26.6	25.7
8	2	14.5	14.5
8	4	45.7	-44.6
8	6	-2.0	5.0
8	8	-2.1	9.7
9	1	6.3	-2.0
9	3	1.5	-9.2
9	5	33.2	33.8
9	5	4.4	0.1
9	7	-2.1	-0.3
9	9	-2.2	-15.0
10	0	38.2	33.9
10	2	18.0	-18.4
10	4	36.6	33.1
10	8	17.3	-17.3
10	8	7.2	-6.9
11	1	27.1	-27.7
11	3	-20.1	-20.6
11	5	7.3	-7.1
12	0	58.2	-56.1
12	2	14.6	15.1
12	6	-2.2	-1.8
12	6	9.8	0.5
13	1	7.2	9.4
13	3	-2.7	-7.5
13	5	-2.4	-6.2
14	0	26.2	6.8
14	2	16.1	-14.9

1	2	43.2	39.1
1	4	26.8	-24.3
1	6	20.0	19.3
1	8	26.5	-26.9
1	10	7.1	7.5
1	12	15.2	15.7
2	1	-8.5	-7.6
2	3	71.7	-72.6
2	5	44.5	46.1
2	7	16.9	-17.2
2	9	-1.9	2.2
2	11	19.9	-21.1
2	13	13.1	13.1
3	2	60.8	58.9
3	4	3.7	-3.0
3	6	41.8	-33.3
3	8	14.7	-14.7
3	10	14.9	15.2
4	1	8.1	-0.8
4	3	17.4	-14.9
4	5	12.5	-13.0
4	7	17.5	19.1
4	9	-2.0	0.5
4	11	7.8	7.6
5	2	30.2	-51.1
5	4	14.0	14.7
5	6	-1.7	6.4
5	8	-1.9	2.4
5	10	47.1	-45.9
5	12	10.0	9.1
6	1	70.3	71.5
6	3	19.5	16.6
6	5	-27.0	-27.4
6	7	37.7	-39.3
6	9	19.2	15.7
6	11	14.9	-15.2
7	2	8.4	6.8
7	4	22.2	21.0
7	6	15.6	15.9
7	8	24.2	-23.9
7	10	17.4	-17.0

h=1

0	0	65.0	-53.6
0	-2	85.6	-77.3
0	2	92.6	90.4
0	-4	49.0	55.1
0	4	70.9	69.3
0	-6	11.3	-10.6
0	6	15.0	-15.9
0	-8	4.3	-1.1
0	8	28.0	-23.1
0	-10	33.6	-34.0
0	10	51.4	53.1
0	-12	19.1	-15.6
0	12	-2.4	12.6
1	-1	54.7	49.2
1	1	12.8	-11.7
1	-3	6.6	-5.1
1	3	37.7	-37.3
1	-5	8.4	-9.4
1	5	46.6	-45.4
1	-7	16.1	17.0
1	7	51.3	55.1
1	-9	7.1	-7.5
1	9	-2.0	-2.1
1	-11	11.4	-10.9
1	11	-2.2	-1.7
1	-13	11.8	-12.0
2	0	12.5	10.5
2	-2	41.8	41.7
2	2	19.2	-19.7
2	-4	19.3	18.9
2	4	23.5	24.7
2	-6	5.5	-2.6
2	6	35.6	-36.4
2	-8	13.5	-12.1
2	8	31.0	34.5
2	-10	25.6	24.5
2	10	34.1	-35.7
2	-12	27.6	-27.2
2	12	21.8	23.7
3	-1	108.1	-105.0
3	1	86.3	81.6
3	-3	70.9	71.5
3	3	12.6	-11.2
3	-5	5.9	5.7
3	5	25.9	26.1
3	-7	9.3	6.4
3	7	39.2	-40.1
3	-9	30.6	32.1
3	9	5.5	-1.5
3	-11	5.5	-1.5
3	11	8.6	8.7
3	-13	14.2	11.8
4	0	-1.2	-2.0
4	-2	20.0	-17.4
4	2	-1.3	3.4
4	-4	52.5	-52.7
4	4	40.9	-43.5
4	-6	10.7	7.2
4	6	29.4	31.8
4	-8	20.0	19.3
4	8	26.5	-25.6
4	-10	10.6	9.9
4	10	9.1	-9.7
4	-12	10.2	-9.0
4	12	11.9	-11.8
5	-1	25.1	26.8
5	1	31.0	-32.4
5	-3	54.4	49.2
5	3	52.2	53.5
5	-5	31.9	30.7
5	5	44.7	-63.0
5	-7	4.8	-4.4
5	7	1.9	6.7
5	-9	7.0	-.9
5	9	8.2	-7.2
5	-11	12.8	12.6
5	11	7.4	-0.4
5	-13	10.3	8.1
6	0	25.2	27.0
6	-2	30.7	-32.7
6	2	6.9	5.3
6	-4	15.3	15.7
6	4	-1.7	-3.6
6	-6	13.2	-8.1
6	6	8.9	1.6
6	-8	6.8	.8
6	8	-2.1	-0.2
6	-10	6.8	-6.2
6	10	-2.3	3.1
6	-12	10.0	6.7
7	-1	5.0	-5.4
7	1	10.5	10.5
7	-3	9.4	10.7
7	3	63.0	-68.1
7	-5	46.0	-48.1
7	5	29.7	29.
7	-7	6.8	6.2
7	7	7.8	-27.7
7	-9	6.1	1.4
7	9	6.1	4.5

8	1	37.7	-38.3
8	3	28.0	28.1
8	5	25.6	-26.5
8	7	45.4	45.5
8	9	22.4	-22.6
8	11	6.6	-7.1
9	2	37.5	37.0
9	4	10.5	10.2
9	6	23.3	-24.0
9	8	16.0	-6.9
9	10	6.5	-1.1
10	9	7.5	-3.6
10	1	10.1	3.7
10	3	31.2	-31.1
10	5	9.2	44.0
10	7	-2.2	-0.4
11	2	35.4	37.0
11	4	6.7	6.3
11	6	8.7	-9.1
11	8	12.5	10.8
12	1	15.7	-15.1
12	3	1.0	1.0
12	5	7.2	-3.5
12	7	6.6	5.2
13	2	6.3	0.1
13	4	7.4	-5.9
14	1	13.7	12.0

7	-11	5.1	2.8
7	11	13.4	-14.6
8	0	31.0	-26.8
8	-2	-1.7	-5.0
8	2	47.9	50.5
8	-4	23.5	22.3
8	4	17.0	16.6
8	-6	39.3	42.5
8	6	32.2	-33.5
8	-8	13.6	-12.3
8	8	6.9	-6.1
8	-10	12.4	-11.0
8	10	10.7	11.2
9	-1	62.1	65.3
9	1	37.2	-36.5
9	-3	12.9	-12.1
9	3	15.1	-14.1
9	-5	10.7	11.2
9	5	21.8	-21.6
9	-7	27.0	-28.0
9	7	29.7	30.7
9	-9	14.7	13.7
9	9	12.4	-11.8
10	0	-1.9	2.1
10	-2	4.4	-4.9
10	2	16.0	-16.5
10	-4	12.1	13.7
10	4	14.7	-16.3
10	-6	16.4	17.2
10	-2	-2.2	-5.1
10	-8	6.2	5.7
10	-10	16.4	-15.1
11	9	6.5	-7.2
11	-3	8.7	9.2
11	3	10.1	11.9
11	-5	29.6	31.2
11	5	9.3	-7.9
11	-7	16.1	17.0
11	7	24.5	-25.4
11	-9	9.4	-12.1
12	1	5.7	3.1
12	0	15.0	15.9
12	2	29.2	31.2
12	2	24.6	-24.6
12	-4	19.4	-20.5
12	-6	8.2	5.0
12	6	-2.4	-0.6
13	-1	5.1	-6.5
13	1	5.1	-5.5
13	-3	6.9	-9.6
13	3	9.2	6.9
14	0	8.5	3.2
14	-2	-2.4	4.1

1	0	10.3	7.4
1	2	98.4	-96.1
1	-2	61.6	-59.9
1	4	27.6	29.8
1	-4	68.0	68.4
1	6	20.7	-22.7
1	-6	63.5	-65.2
1	8	17.7	18.5
1	-8	37.5	40.4
1	-10	-2.0	2.2
1	10	4.7	-4.7
1	-12	20.4	21.0
1	12	4.8	8.6
2	1	38.1	35.1
2	3	17.5	-14.3
2	3	25.1	-25.5
2	-3	74.5	-73.3
2	5	31.4	-30.4
2	-5	6.5	6.6
2	7	20.4	19.5
2	-7	24.4	24.7
2	9	30.4	31.6
2	-9	4.8	4.2
2	-11	21.8	-21.3
2	11	10.6	-11.3
2	-13	-14.4	-12.6
3	0	149.1	-148.2
3	2	23.7	-22.2
3	-2	87.3	85.8
3	4	68.3	63.5
3	-4	17.4	16.1
3	6	32.8	34.8
3	-6	27.3	28.1
3	8	8.0	-9.8
3	-8	26.2	-27.5
3	-10	8.5	-5.4
3	10	4.6	-5.8
3	-12	10.6	9.0
4	1	10.9	12.1
4	1	55.8	44.7
4	-1	18.2	-17.0
4	3	64.4	-64.2
4	-3	6.9	5.7
4	5	7.7	5.9
4	-5	9.4	-7.6
4	7	22.3	-23.6
4	-7	10.8	10.4
4	9	43.1	44.1
4	-9	12.5	-11.8
4	11	15.4	-16.0
4	-13	12.4	11.4
5	0	40.0	40.0
5	2	20.1	20.5
5	-2	29.6	29.4
5	4	13.6	14.0
5	-4	26.4	25.3
5	6	12.3	-11.7
5	-6	15.4	15.2
5	8	13.1	26.4
5	-8	21.5	23.4
5	10	6.3	-7.5
5	-10	14.9	-12.1
5	-12	18.0	-17.6
6	1	40.6	-41.3
6	-1	70.0	68.3
6	3	66.5	65.6
6	-3	47.3	47.9
6	5	30.8	29.0
6	-5	8.3	-7.0
6	7	28.9	29.8
6	-7	-1.8	3.6
6	9	18.0	-20.1
6	-9	14.4	-15.4

6	-11	15.0	15.4
6	11	17.7	15.9
7	0	36.3	-34.1
7	2	43.7	44.0
7	-2	22.6	20.4
7	4	16.6	-19.1
7	-6	9.3	9.2
7	6	8.1	7.2
7	-6	37.1	38.3
7	8	-2.1	0.1
7	-8	4.5	-2.0
7	-10	6.0	-3.4
7	10	7.3	-6.5
7	-12	-2.4	-9.1
8	-1	40.5	40.9
8	1	23.2	24.0
8	3	14.9	-15.4
8	5	8.8	-9.9
8	5	10.2	10.7
8	-5	-1.9	-5.1
8	7	26.4	-27.6
8	-7	11.4	-12.2
8	9	25.8	25.0
8	-9	30.5	30.7
9	0	34.0	-31.4
9	-2	9.4	8.7
9	2	39.0	38.2
9	4	21.3	21.0
9	-4	-1.9	4.4
9	6	27.4	26.3
9	-6	-2.0	3.1
9	8	13.9	-12.5
9	-8	23.5	-24.1
10	0	5.2	2.3
10	-9	13.3	-11.4
10	1	4.4	2.1
10	-1	5.3	-7.1
10	3	11.5	11.4
10	-3	14.0	-13.8
10	5	44.9	-45.2
10	-5	16.0	-15.5
10	7	11.4	11.7
10	-7	23.7	23.7
11	-8	12.9	12.0
11	2	49.7	-51.1
11	-2	24.2	-24.3
11	4	28.3	27.6
11	-4	26.8	26.5
11	6	8.9	-9.6
11	-6	21.9	-23.2
12	1	7.7	8.2
12	-1	8.4	-8.6
12	3	-2.2	-5.4
12	-3	6.0	1.4
12	5	8.2	6.3
12	-5	5.1	-2.1
13	0	13.0	-11.9
13	2	14.5	-12.1
13	-2	15.5	15.1
13	4	21.4	-20.9
13	-4	25.1	-24.3
13	-6	15.2	18.7
14	-1	22.9	-24.8
14	-1	-2.4	-3.1
14	-3	13.8	13.5

h=2

0	0	207.7	-214.1
0	-2	121.6	124.4
0	2	86.9	-92.2
0	4	21.6	20.1
0	-4	13.5	-13.6
0	-6	130.0	100.6
0	6	62.5	55.9
0	-8	36.6	-36.4
0	-10	26.0	27.0
0	10	14.0	14.7
0	-14	17.4	18.5
0	-14	13.7	-14.8
1	-1	57.2	-51.7
1	1	53.7	-52.6
1	-3	84.2	-81.8
1	3	42.4	-42.2
1	-5	30.0	-29.1
1	5	33.2	-34.4
1	-7	17.1	17.0
1	7	11.8	-12.3
1	-9	28.3	27.4
1	9	32.9	36.1
1	11	42.8	-44.2
1	-11	8.3	5.0
1	-13	-2.1	-1.9
1	13	18.2	-17.0
2	0	71.5	-65.3
2	2	57.4	-57.1
2	-2	59.7	-55.0
2	-4	11.0	11.6
2	4	13.6	15.7
2	-6	6.9	3.1
2	8	14.1	14.9
2	-8	7.7	6.3
2	10	14.3	-14.2
2	-10	12.2	12.5
2	-12	18.5	-19.8
2	12	12.7	-12.6
3	-1	48.2	45.9
3	1	22.5	-23.2
3	-3	61.2	64.1
3	3	19.5	-19.0
3	-5	29.6	30.3
3	5	9.5	-9.7
3	-7	46.8	45.1
3	7	24.8	26.4
3	-9	9.3	6.3
3	9	16.9	-16.9
3	-11	29.6	30.3
3	-13	8.4	6.6
4	0	50.1	-46.6
4	-2	11.0	-10.8
4	2	29.4	28.6
4	-4	24.9	24.7
4	-6	37.3	38.9
4	6	21.2	-23.7

4	-8	4.7	2.1
4	8	14.9	16.7
4	-10	35.4	-35.2
4	10	9.6	10.1
4	-12	13.0	-12.6
5	-1	7.5	10.0
5	1	33.2	30.4
5	3	-2.5	1.8
5	-3	36.0	-37.5
5	-5	8.7	-7.8
5	5	44.4	43.9
5	-7	25.2	-26.5
5	7	12.2	-13.3
5	-9	17.9	18.5
5	-11	10.8	-11.4
5	-13	6.2	3.0
6	0	7.8	3.1
6	-2	16.7	15.1
6	4	4.0	-2.8
6	-6	5.6	-4.4
6	6	10.3	10.8
6	8	29.3	29.7
6	-8	4.8	0.0
6	-10	11.7	-6.7
6	10	6.5	3.6
6	-12	6.1	1.1
7	-1	9.8	-10.4
7	1	26.4	-27.2
7	-5	13.8	13.8
7	5	40.9	-42.2
7	-7	30.7	32.5
7	7	-2.1	3.0
7	-9	27.8	-26.9
7	9	6.3	-5.4
7	-11	11.4	10.9
8	0	6.9	8.0
8	2	-1.8	-2.5
8	2	60.9	-60.3
8	-4	18.5	14.2
8	-6	18.1	-20.6
8	-8	24.0	23.0
8	-8	8.7	-5.7
8	-10	-2.1	6.4
9	-1	28.6	-28.0
9	1	14.8	15.7
9	-3	-1.9	-1.1
9	3	-2.0	2.3
9	-5	-2.0	6.6
9	5	12.5	-11.8
9	7	5.7	6.6
9	-7	14.3	14.3
9	-9	16.4	19.2
9	-11	13.2	-13.4
10	-2	16.3	15.8
10	2	14.1	13.1
10	-4	18.2	-20.1
10	-6	38.6	39.5
10	6	9.5	9.4
10	-8	6.2	3.6
10	-10	9.3	8.4
11	-1	14.8	15.8
11	1	35.5	-35.9
11	-3	13.8	15.3
11	5	10.3	9.8
11	5	12.4	13.2
11	7	10.2	-9.4
11	-9	-2.4	-1.3
12	0	28.0	26.9
12	-2	29.9	-28.3
12	-4	18.1	20.1
12	4	8.8	8.5
12	-6	9.0	0.4
13	-1	8.2	5.7
13	1	10.5	10.1
13	-3	15.2	13.6
13	3	6.6	-8.5
13	-5	7.6	4.8

4	5	37.6	37.4
4	5	9.9	8.1
4	7	5.4	-5.4
4	9	10.4	12.2
4	-9	5.7	6.4
4	-11	7.8	-7.0
4	-13	14.6	-8.9
5	0	31.1	-30.7
5	2	6.5	8.3
5	-2	25.9	-24.4
5	-4	-1.7	-1.8
5	-4	14.3	15.1
5	8	26.3	-28.0
5	-10	35.6	-37.4
5	10	23.0	24.8
5	-12	15.3	15.1
6	1	8.7	-9.4
6	-1	46.4	50.6
6	3	18.1	-19.6
6	-3	26.4	-28.3
6	5	27.1	-29.6
6	-5	26.1	-26.0
6	-7	36.5	35.9
6	-7	12.0	-12.1
6	-9	9.4	8.1
6	-9	6.4	8.0
6	-11	11.1	-10.7
7	0	-1.7	0.4
7	2	4.8	-5.3
7	-2	52.4	51.8
7	4	-1.9	0.2
7	-4	5.0	-6.3
7	6	4.5	4.6
7	-6	4.1	2.1
7	-8	5.0	-3.1
7	-8	23.0	-24.9
7	10	22.6	-23.4
7	10	17.5	17.2
7	-12	16.1	9.3
8	1	34.4	38.8
8	-1	36.1	-36.7
8	3	22.2	-20.2
8	-3	15.2	17.2
8	-5	24.6	25.1
8	-5	4.2	5.7
8	-7	5.0	-25.0
8	9	7.0	7.5
8	-9	21.6	-23.4
8	-11	13.4	-13.8
9	0	14.9	14.2
9	2	21.3	-21.6
9	-4	31.6	-32.2
9	-2	-2.2	-1.6
9	4	9.8	9.8
9	-10	5.9	-6.1
10	1	25.9	-25.0
10	1	12.6	12.8
10	3	28.6	28.7
10	-3	16.9	-18.0
10	5	9.2	-9.3
10	-5	26.0	26.7
10	-7	11.8	-8.7
10	-7	-2.2	1.6
11	2	10.2	-11.2
11	-2	6.6	6.1
11	4	16.3	-17.3
11	6	16.9	18.9
11	-6	18.8	10.0
12	-1	16.9	-18.0
12	1	-2.2	1.7
12	3	6.0	-4.9
12	-3	13.2	-13.7
12	5	24.4	-24.6
12	-5	-2.3	1.9
12	-7	11.3	10.9
13	0	13.8	-11.4
13	2	10.6	-8.8
13	-2	10.8	10.8
13	-4	7.5	4.6

h=3

0	0	72.0	7.3
0	-2	96.9	104.8
0	2	52.4	50.6
0	-4	97.5	-97.5
0	4	45.5	-43.9
0	-6	71.6	73.2
0	6	4.2	-6.1
0	-8	31.6	31.5
0	8	51.5	52.9
0	-10	44.2	46.2
0	10	9.8	-5.0
0	-12	16.5	-10.8
0	-14	17.2	15.8
1	0	5.6	-16.0
1	-2	10.0	-8.6
1	2	21.0	-22.5
1	-5	39.2	37.7
1	5	47.0	41.7
1	-2	4.9	3.5
1	7	22.3	-23.7
1	9	3.8	6.9
1	-9	20.9	-21.9
1	-6	16.1	-16.7
1	-13	10.6	11.7
2	-2	64.8	-65.8
2	2	12.1	-12.5
2	-4	41.0	40.2
2	4	34.5	-36.3
2	-6	13.3	-13.6
2	6	15.2	15.9
2	-8	31.3	31.3

2	8	24.8	-27.0
2	-10	15.8	-15.9
2	-10	12.4	12.0
2	-12	32.2	32.5
2	-14	-2.3	-0.2
3	-1	48.7	49.9
3	1	10.4	-9.6
3	-3	48.2	-45.2
3	3	42.3	40.0
3	-5	22.1	-22.9
3	-7	15.9	17.9
3	7	31.3	11.5
3	-9	9.6	8.1
3	-11	8.3	-8.3
3	-13	18.7	-20.0
4	0	7.6	1.3
4	-2	13.7	14.2
4	2	48.6	-47.5
4	-4	15.3	14.0
4	-6	13.4	-13.8
4	6	-2.0	0.6
4	8	56.5	-58.0
4	8	6.0	5.7
4	-10	5.3	6.1
4	10	9.4	-9.5
4	-12	22.5	19.3
5	-1	51.6	-51.2
5	1	31.3	31.4
5	-3	13.5	-12.8
5	3	34.0	-34.8
5	5	2.9	2.5
5	-7	15.1	15.3
5	7	17.1	-18.5
5	-9	24.0	23.9
5	9	9.8	9.0
5	-11	30.4	-31.0
6	0	7.2	5.3
6	-2	19.4	17.1
6	-2	6.4	6.6
6	-4	-1.8	-3.5
6	-6	11.4	8.8
6	6	4.3	-3.0
6	-8	8.8	8.3
6	-10	8.7	-8.7
6	-12	4.9	-2.1
7	1	14.9	-14.7
7	-3	10.1	-10.0
7	-5	18.3	19.4
7	-7	14.8	-14.5
7	7	11.2	10.3
7	-11	14.9	14.6
8	-2	18.5	13.9
8	2	7.6	-8.1
8	4	6.9	-9.1
8	4	21.0	-21.4
8	6	12.9	-13.8
8	-6	-2.2	-2.9
8	-8	10.0	5.3
8	-10	11.3	11.2
9	1	39.9	-40.4
9	-1	18.1	19.1
9	-3	11.3	14.8
9	5	-2.0	-1.8
9	5	25.6	27.0
9	-7	21.2	22.4
9	-9	6.5	1.5
9	-9	15.1	-14.4
10	0	18.3	-19.6
10	-2	11.3	11.3
10	-4	16.2	-17.2
10	-6	16.3	25.3
10	-6	7.6	7.5
10	-8	16.4	-16.0
10	-10	22.6	21.0
11	-1	8.5	8.5
11	-3	17.5	-17.9
11	-5	6.6	-5.8
11	-7	8.6	13.3
11	-9	10.6	10.6
12	0	19.1	14.3
12	2	6.4	4.1
12	-4	14.5	14.4
12	-6	17.1	-16.1
13	-1	-2.4	-2.6
13	-3	8.4	-10.5
13	-5	7.7	-7.3

1	0	3.0	-1.8
1	2	4.1	1.4
1	-2	7.1	8.5
1	-4	25.9	-25.9
1	-6	-1.9	-4.3
1	-6	34.2	35.6
1	8	-2.1	-3.6
1	-8	37.8	-37.8
1	-10	5.7	-5.0
1	-12	45.5	-22.5
1	-14	21.4	20.9
2	-1	12.5	10.0
2	-1	12.5	13.5
2	-3	-2.6	-0.2
2	-5	-1.8	-2.6
2	-7	19.5	20.6
2	-9	49.2	-50.0
2	-9	23.0	23.4

Table 15 (Continued)

Column 1:

```
2 -11    8.6    8.3
2 -13    8.4   -7.7
3  0    47.4   42.2
3  2    55.5   56.1
3 -2    -1.4   -2.1
3 -4     4.8    5.5
3 -4    51.9  -28.2
3  6    16.3  -16.4
3 -6     9.7   -2.7
3  8     7.6   -8.3
3 -8    29.0   29.9
3 -10   14.9  -14.0
3 -10   13.6   12.0
3 -12    5.7   -4.1
3 -14   15.0   15.8
4 -1    47.2  -47.9
4 -1     5.3   -7.0
4 -3    27.4   26.6
4 -3    26.7  -28.4
4  5    19.5  -20.0
4 -5    20.0   20.4
4  7     8.1    8.2
4 -7    34.0  -34.6
4 -9    12.1  -12.0
4 -9    35.1  -34.7
4 -11   26.9   25.4
4 -13   16.9  -10.4
5  0    12.9   10.6
5  2    30.7  -29.3
5 -2     4.3   -3.4
5  4    30.4  -30.1
5 -4    12.8  -12.9
5  6    16.0   15.1
5 -6    54.0  -56.3
5  8     6.1   -4.9
5 -8     4.2   -2.0
5 -10   14.9   15.5
5 -12    5.9    4.4
6  1    16.2   16.5
6 -1    42.3  -42.0
6  3    14.9   15.2
6 -3    -1.7   -0.6
6 -5    -2.0   -3.0
6 -5    21.6   23.5
6  7    30.4  -33.5
6 -7     7.3   10.0
6 -9    15.0   11.5
6 -9     9.7  -55.0
6 -11   20.5  -21.6
6 -13   29.6   29.0
7  0     5.6    4.0
7  2    18.2  -17.8
7 -2    28.7  -28.6
7  4    27.1  -28.4
7 -4    27.6  -27.6
7  6    10.2   -8.5
7 -6    28.6   29.2
7  8     6.4    5.8
7 -8     5.5   -3.8
7 -10   24.9   26.1
7 -12    8.4   -9.1
8 -1    25.6  -25.5
8 -1    17.6  -19.1
8  3    12.3  -14.6
8 -3    10.5   10.3
8 -5    -2.1    1.1
8 -5    12.4  -12.5
8  7     9.6    9.7
8 -7     9.1    8.9
8 -9    26.2  -26.9
8 -11   20.6   18.8
9  0    17.9   16.8
9  2    20.9   19.9
9 -2    27.1  -25.8
9  4     7.6    7.9
9 -4    27.6   27.8
9 -6    16.6  -16.1
9 -6     6.5    4.0
9 -8    16.9   17.0
9 -10   13.8  -12.4
10 -0   25.9   26.6
10 -1    5.8   -3.3
10 -1   13.6   14.3
10 -3   -2.1   -1.7
10 -5   -2.1   -0.6
10 -7   24.5  -24.5
11 -0   15.4  -14.6
11 -0   12.4  -13.4
11 -2   26.7   27.4
11 -2   11.3   11.0
11 -4    6.4   -6.2
11 -6   22.4  -22.7
11 -6   21.1   21.1
12 -0    8.9    8.1
12 -1   -2.3    2.0
12 -3    7.6    7.5
12 -3   10.8   12.0
12 -5   14.7   14.4
12 -7    5.4    5.0
13 -0   16.5   16.9
13 -2    6.5    3.9
13 -4   -2.4    4.0
```

h=4

```
0  0    60.7   61.4
0 -2    50.1  -51.8
0 -2    40.9   43.6
0 -4    14.0  -11.4
0  4    41.9   41.8
0 -6     6.3   -9.4
0 -6    35.2  -36.6
0 -8   -14.7   20.4
0  8     6.8   -7.9
0 -10    7.2   -6.2
0 -12   28.2   27.7
0 -14   17.0   12.3
1 -1     7.3    8.1
1 -1    33.4   35.3
1 -3    47.7   48.0
1 -3    21.2  -22.7
1 -5    30.6  -29.4
1  5    12.1   12.7
1 -7    21.4  -18.4
1 -7    -2.2    9.3
1 -9    -1.8    4.0
1 -9     5.3   -2.1
1 -11   16.0   16.4
1 -13   11.7  -11.1
```

Column 2:

```
2  0    23.5   23.0
2 -2    24.5   24.9
2  2    44.5   45.6
2 -4    17.5  -19.1
2 -4    11.2   -2.1
2 -6    25.7  -25.7
2  6    26.0   24.7
2 -8     4.7    2.3
2  8    14.0  -15.3
2 -10   15.0   15.5
2 -12    8.1    8.8
2 -14   -2.3   -3.0
3 -1    10.2  -12.9
3  1    22.8  -23.2
3 -3    35.8  -35.4
3  3    35.6   35.9
3 -5    47.0   48.0
3  5     8.4   -9.2
3 -7    26.6  -26.1
3 -7    17.1  -16.6
3 -9     7.1   -3.9
3  9    -2.4   -3.8
3 -11    7.1    4.5
3 -13   34.5   33.6
4  0    28.9   23.0
4 -2     7.8   -8.8
4 -2     7.0   -4.1
4 -4    43.7  -33.4
4  4    -2.0   -0.7
4  6    49.9  -51.0
4 -6    14.7  -14.3
4 -8    38.3   43.8
4  8    15.7  -12.3
4 -10   27.8   29.5
4 -12   19.8  -17.3
5 -1    22.1  -24.4
5 -1    -1.8    3.8
5 -3     8.2    8.4
5 -3     5.3    5.3
5  5    13.2   13.8
5  5     5.7    4.6
5 -7     5.2    4.7
5 -7    -2.3    6.4
5 -9    34.2  -34.5
5 -11   18.1   17.1
5 -13    9.5    5.8
6  0    17.9  -16.4
6 -2    -1.8    0.1
6  2     8.1    0.2
6 -4     8.1   -8.6
6 -6     6.2    2.9
6  6     7.9   -8.0
6 -8    18.0  -19.5
6  8    -2.4    2.5
6 -10   17.5   17.4
6 -12    8.6    1.4
7 -1    23.7   20.9
7  1     2.0   -0.3
7 -3    23.0  -24.6
7  3    16.6  -17.5
7 -5    19.7  -17.6
7 -5    -2.2    0.9
7  7     5.3    2.9
7 -7    40.5   41.6
7 -11   22.2  -22.2
8  0     7.6   -6.5
8 -2    13.9  -14.0
8  2    35.1   35.3
8 -4     8.3   10.2
8  4    16.7   16.9
8 -6    21.9   23.5
8 -8    21.3  -21.6
9 -1    -2.1   -5.2
9  1     8.2    8.4
9 -3    18.4   20.2
9  3     9.3   -8.0
9 -7    -2.2    2.9
9 -9     8.9   -7.5
10 -0   10.4    9.6
10  2   15.1  -16.0
10 -4    9.2    8.0
10 -6   14.1  -18.2
10 -8   -2.5   -1.5
11 -1   16.8  -16.1
11 -1   14.1   12.7
11  3    8.0   -7.2
11 -5    5.1    2.6
11 -7    8.3   -5.9
12 -0   22.0  -20.5
12 -2   19.0   17.4
12 -4   29.2  -28.3
12 -6   -2.4   -3.8
```

Column 3 (continued from column 2 lower section):

```
1  0    -1.6   -2.4
1 -2    18.4  -20.1
1 -2    57.3   58.5
1  4    14.2   14.5
1 -4    -1.5   -1.1
1  6    -2.1   -8.0
1 -6    28.1   27.6
1  8    -1.6    2.0
1 -8   48.4  -47.3
1 -10  67.1   70.6
1 -12  12.7  -14.4
2 -1    -9.4   -7.1
2 -1   21.8   21.4
2  3   34.7  -35.2
2 -3   10.9  -10.6
2 -5   25.8  -28.1
2  5   22.0  -20.6
2 -5   62.3  -63.6
2 -7    2.2   -4.7
2  7   47.4   47.5
2 -9   11.4  -11.7
2 -11  39.5  -40.6
2 -13  33.4  -33.4
3  0   34.5  -32.5
3  2   11.0  -10.8
3 -4   13.8  12.5
3 -4   -1.9   -7.6
3 -4   52.0  -52.2
3 -4   24.1  -23.0
```

h=5

```
0  0    -1.8    6.8
0 -2    12.5   12.6
0 -2    10.0  -16.0
0 -4    -1.6   64.7
0 -6    30.9   32.5
0 -6    76.0  -76.8
0 -6    21.0   20.1
0 -8   -1.8  -14.0
0  8   14.9   14.6
0 -10  32.5  -27.5
1 -1   17.6   17.6
1 -1   17.0   17.5
1 -3   38.6  -37.9
1  3    6.3   -7.1
1 -5    9.5   -8.3
1  5   18.0  -11.8
1 -7    5.6    5.1
1 -7   -2.3    0.7
1 -11  18.2  -18.6
1 -9    6.9    6.0
2 -0   -1.8   -5.2
2  2   -1.6    2.0
2  2    9.1  -10.6
2 -4   31.5  -32.8
2 -4   14.7   16.7
2 -6    5.5    4.7
2 -8   28.7  -25.0
2 -10  17.4   17.0
2 -12  26.8  -26.8
3 -1   11.1   13.0
3  1   12.6   13.2
3 -3   58.5   59.2
3  3   26.1  -27.0
3 -5   23.3   23.2
3  5    7.0    2.5
3 -7    5.1   -0.0
3 -7   14.7   13.8
3 -11  13.0   -1.8
4  0   13.0   -6.8
4 -2   27.2  -28.0
4  2   36.7   36.9
4 -4   -1.8    6.3
```

Column 4:

```
4  4    -2.1    0.9
4 -6    38.6   40.7
4  6     6.3    2.6
4  4    20.0   21.7
4 -10   43.8  -44.8
4 -12   15.9   13.0
5 -1    37.4   36.1
5  1    45.1  -45.7
5 -3    14.0  -14.5
5  3     9.4    9.3
5 -5    22.0  -11.6
5  5    12.0  -11.9
5 -7    41.0  -41.3
5 -9    29.4   30.3
5 -11   15.9   16.7
6  0    12.7   12.8
6 -2     6.2    7.5
6  2    -2.1    2.7
6 -2     8.2  -10.7
6  4     5.0    6.2
6 -4    17.6   18.3
6  6     6.5    2.6
6 -8    -2.1   -0.7
6 -10   15.4   15.1
6 -12    8.0   -6.2
7  1    35.8  -36.6
7 -1    36.7   35.4
7 -3    21.6   20.7
7  3    -6.1   -6.1
7 -5    15.5  -16.5
7  5    10.6    7.6
7 -7    27.8   26.9
7 -9    22.5  -21.1
7 -11    8.4   -6.6
8  0    21.2  -21.1
8  2    16.6  -13.5
8 -2    14.9   15.6
8  4    11.0  -10.2
8 -4     5.3   -2.9
8 -6    23.0  -24.4
8 -8    13.2  -13.4
8 -10    9.1    7.2
8 -10   10.1   31.1
9  1    15.1  -35.4
9 -1    -2.3   -3.2
9  3     8.4    8.6
9 -5    26.0   26.5
9 -7    24.6  -24.3
9 -9     8.2    7.6
10  0    8.2    7.8
10 -2   -2.3   -2.0
10  2    9.5    9.5
10 -4   14.8   15.8
10 -6   11.0  -10.4
10 -8   11.0   10.9
11 -1    7.5   -6.1
11 -3   26.6   27.6
11 -5   19.5  -19.2

1  0    54.9   55.3
1  2    23.1  -23.8
1 -2    28.3  -25.7
1 -2    15.0   15.8
1 -4    10.4   13.5
1 -6    12.4  -13.2
1 -6    15.3  -15.0
1 -8    51.0   54.3
1 -10   26.0  -22.4
1 -12    8.7   -8.0
2 -1    17.9  -18.1
2  1   -1.8    2.9
2 -3    49.3  -48.8
2  3     8.4   -8.1
2 -3    24.7   24.5
2 -5    6.9   -3.4
2 -7    10.1   11.0
2 -7   -2.4   -8.1
2 -9    -1.8   -1.6
2 -11   31.2   31.7
2 -13   18.5   -5.7
3  0    18.5  -19.2
3  2    -2.0   -4.2
3  4    43.7   44.4
3  4    29.1  -28.9
3 -6    17.9  -17.4
3  6    14.0   14.2
3 -8    34.4   36.8
3 -10   12.2   11.0
3 -12   16.8   -7.8
4 -1    23.5   24.4
4  1     7.2    8.7
4 -3    10.8  -11.0
4  3    -1.8   -3.0
4 -5    14.9   14.6
4  5    -1.9    3.0
4 -7    -2.2    2.2
4 -7    11.0   13.5
4 -9    19.1   19.1
4 -11   21.4  -21.7
5 -1    -1.8    6.4
5 -3    18.0  -17.0
5  1    15.0  -12.1
5 -2    7.2   -8.8
5 -4    27.6   27.0
5  4    37.3   37.6
5 -6    18.7   19.7
5 -6    25.6  -27.0
5 -10   18.6   -8.5
6 -1    19.4   14.7
6  1    35.1   36.2
6 -3    23.5  -14.1
6 -3    4.4    4.0
6 -5    -6.5   -1.7
6 -5    26.1  -29.2
6 -9    13.2   12.7
6 -11    7.3    2.4
7  2     7.6   -6.0
7 -2    4.8    6.9
7 -4   14.5   15.4
7  4   31.7   32.5
7 -6   -2.2   -7.9
7 -8   29.8  -35.9
8 -1    13.0   18.9
8 -1   -2.2   -1.1
8 -3   18.0   18.4
8 -3    9.6   10.2
```

Column 5:

```
8 -3    21.2  -25.6
8  5     5.4    5.2
8 -5    11.6   10.0
8 -7     9.8   -9.8
8 -9    16.2   15.0
8 -11   16.3  -15.9
9  0    10.6    9.3
9  2    -2.3   -2.1
9  4     8.5   10.7
9  4    16.3  -15.3
9 -6    13.2   13.7
9 -8     9.7   10.4
9 -10   -2.4    3.0
10  1    6.4   -3.6
10 -1   24.5  -22.4
10 -3   16.0   16.5
10  5    7.2    5.6
10 -7    7.4   -6.3
11  0   16.5   13.4
11 -2   -2.3   -3.7
11 -4    6.5   -5.2
11 -6   10.7   -9.7
```

h=6

```
0 -2    19.2  -16.2
0 -2    -1.8    2.5
0  2    -2.1   -3.0
0 -4    24.4  -25.3
0  4    48.5  -49.8
0 -6    29.5   28.6
0  6    12.7   10.6
0 -8    20.0  -23.5
0 -10   28.3  -27.4
0 -12   20.2  -15.9
1 -1    -2.0    0.2
1 -3    28.5  -25.5
1  3    12.9   13.0
1  5    6.0   -8.2
1 -5   12.0   11.8
1  5    7.4   -0.7
1 -7   11.6  -12.5
1 -9    7.6    8.1
8 -1   14.8   13.8
8 -1   18.7  -20.0
8 -3   21.3   21.7
8 -7    6.3    5.1
9  0   18.9  -21.4
9  2    8.4    6.6
9 -4    5.2    3.1
9 -4   13.2   12.8
9 -6   13.9   -2.7
9 -8   25.8  -28.1
9 -10   27.9   28.3
10  3    8.5   -6.4
10 -5    6.6   -4.9
```

Column 6:

```
2 -11    9.6   -8.0
2 -11   15.0  -15.1
3  0    25.6   24.6
3  2    13.6   11.8
3 -2    22.8  -22.9
3  4    10.2    8.9
3 -4    15.2   15.9
3 -6    18.4   17.3
3 -8    14.3  -14.5
3 -10   14.8   11.2
3 -12    7.9   -3.8
4  1    14.6   13.9
4 -1    36.2  -36.0
4  3    10.0   -8.7
4 -3    34.1   13.4
4 -3    13.1   12.7
4 -5    24.9  -24.0
4 -7    22.7   22.6
4 -9    16.3  -15.2
4 -11    9.2    8.2
5  0    -2.1    1.9
5  2     6.1   -4.8
5  2    20.9   27.3
5 -4    12.9  -12.9
5 -4    19.2  -19.7
5  6    18.0  -18.2
5 -8     4.8   -5.4
5 -10    4.8   -0.8
5 -12    6.3   -6.8
6  1     5.0    4.3
6 -1     7.6    7.2
6  3    32.8   31.7
6 -3    28.7  -28.2
6 -5    53.2   53.8
6 -7    38.1  -39.3
6 -9    13.9   -2.7
6 -11   18.9  -18.8
7  0     7.9    8.5
7  2    -2.3   -4.0
7 -4    22.4   23.1
7 -4    19.4  -19.1
7 -8    23.6  -23.7
7 -8     5.3   -3.4
7 -10   -2.4    1.5
8  1    14.8   13.8
8 -1    18.7  -20.0
8 -3    21.3   21.7
8 -7    6.3    5.1
9  0   18.9  -21.4
9  2    8.4    6.6
9 -4    5.2    3.1
9 -4   13.2   12.8
9 -6   13.9   -2.7
9 -8   25.8  -28.1
9 -10   27.9   28.3
10  3    8.5   -6.4
10 -5    6.6   -4.9
```

h=7

```
0 -2    19.7  -18.3
0  2    5.4   -3.3
0 -4    9.0    6.0
0  4   18.1   19.0
0 -6   11.7    9.4
0 -10  25.4   23.8
0 -12    8.0    6.4
1 -1     4.8    5.3
1 -1    -2.0   -0.6
1 -3     6.2    0.1
1 -5    -2.0    2.3
1 -7     9.7   10.6
1 -9    16.5   17.9
2  0    11.1  -11.1
2 -2    -9.6    8.3
2 -4    7.3    2.8
2 -4    4.7   -4.8
2 -6    11.1   -7.3
2 -8   -2.1  -14.1
2 -10   4.9   -2.0
3  1    20.6  -20.3
3 -1    11.4  -12.8
3 -3    9.0   -7.1
3  3    11.4   10.7
3  7    21.6   21.4
3 -7    10.9  -12.4
3 -9    -2.2   -3.8
3 -11   -2.3   -2.1
4  0    31.1   33.0
4 -2    -2.2    3.6
4 -4    13.0  -13.4
4 -6    20.4  -18.4
4 -8    14.3  -14.1
4  0    13.4   14.2
4 -2    -2.1   -0.5
4 -4   13.7   12.6
5 -1    31.8  -29.8
5 -3    18.0   13.2
5 -5     5.0   -1.3
5 -7    -2.3   -2.5
5 -9    28.4  -29.6
6 -2    7.5   -5.2
6 -4    5.1    5.9
6 -6    0.8    9.5
6 -6    6.3   -2.8
6 -8    6.4   -3.1
7 -1    28.6   28.6
7 -3    18.5  -16.8
7 -5   16.2    2.7
7 -7    8.4    7.8
8 -1    8.5   -0.5
8 -4   22.4   21.8
8 -6   -2.4   -3.3
```

h=8

```
0  0    16.1   16.7
0 -2     4.9    2.0
0 -4    13.5  -11.7
0 -6    14.0  -16.9
0 -8    18.3   17.2
0 -10   18.6   16.9
1 -1     8.4   -9.5
1 -1     4.9   -3.8
1 -5     6.7    8.1
1 -7     8.6    7.5
1 -9     -2.2   -3.4
2 -0    10.8  -10.4
2 -2    11.7   11.1
2 -4    24.3  -22.7
2 -6     6.0    4.1
2 -8    10.7   10.7
3 -1    11.6    6.2
3 -3     5.3   -0.7
3 -5    -2.3   -3.6
3 -7    12.1  -11.1
3 -9    17.4   16.0
4 -4    27.1  -28.2
4 -6    13.5   17.2
4 -8    18.3   15.9
5 -3    -2.4    3.5
5 -5    19.7  -17.0
5 -7    -2.4    4.3

1  0    12.0   11.3
1 -2     9.0   -6.4
1 -4    23.5  -23.1
1 -6     6.9    5.3
1 -6    -2.2   -3.2
2 -1    10.6   -9.1
2 -3    13.8   14.8
2 -5     4.3    0.5
2 -7    16.9  -16.1
2 -9     9.2   -6.2
3 -6    -2.3   -0.3
3 -8     8.0    7.7
4 -5     6.5    3.9
4 -7     5.3   -4.9
5 -4    14.7   14.3
5 -6    -2.4   -1.0
```

the distance between N(18) and the plane is 1.20 Å whereas that of

C(15) is only 0.95 Å.

The bond distances and valency angles of the histamine ion are

given in Table 16, together with the corresponding values obtained by

Donohue and Caron (19) for histidine. The bond lengths of the two

analyses are in good agreement except for the C(12)-C(13) bond in

histidine which is significantly longer than the analogous bond in

histamine. Since the carboxyl group is attached to the C(12) of

histidine, the increase in the C(12)-C(13) bond is not surprising.

Considering the hydrogen bonding scheme, the probable tautomers

of the imidazole ring are:

| I | II | III | IV | V |
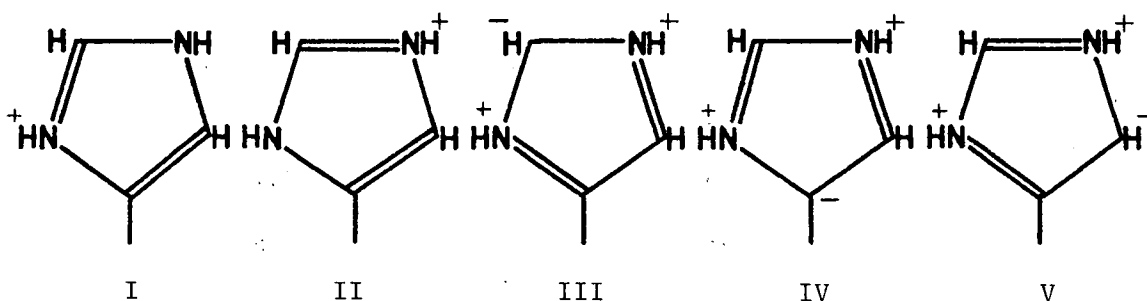
Upon applying the carbon-nitrogen bond-order-length equation (20)

$$r_x = r_1 - (r_1 - r_2)(3x)/(2x + 1)$$

where r_1 = single bond length, r_2 = double bond length, r_x = observed

bond length, and x = percent double bond character to the observed

carbon-nitrogen bond lengths in the imidazole ring, the C(14)-N(18),

C(15)-N(16), C(17)-N(16), and C(17)-N(18) bonds were found to have

Table 16

Bond distances (Å) and valency angles (degrees)

Standard deviations

σ(P-O)	0.009	σ(O-P-O)	0.5
σ(C-N)	0.018	σ(< at C,N)	1.0-1.2
σ(C-C)	0.020		
σ(C-H)⎤		σ(X-Y-H)	9
σ(N-H)⎬	0.15	σ(H-X-H)	12
σ(O-H)⎦			

	Histamine ion	Histidine
C(12)-N(11)	1.494	1.495
C(12)-C(13)	1.490	1.527
C(13)-C(14)	1.498	1.508
C(14)-C(15)	1.346	1.358
C(14)-N(18)	1.379	1.386
C(15)-N(16)	1.383	1.359
C(17)-N(16)	1.311	1.314
C(17)-N(18)	1.336	1.319
N(11)-C(12)-C(13)	111.0	
C(12)-C(13)-C(14)	114.9	
C(13)-C(14)-C(15)	130.9	
C(13)-C(14)-N(18)	122.5	
C(15)-C(14)-N(18)	106.4	
C(14)-C(15)-N(16)	107.5	
C(15)-N(16)-C(17)	108.6	
C(14)-N(18)-C(17)	108.6	
N(16)-C(17)-N(18)	108.8	
N(11)-H(20)	1.06	
N(11)-H(21)	0.94	
N(11)-H(22)	0.98	
C(12)-H(23)	1.13	
C(12)-H(24)	1.04	
C(13)-H(25)	1.05	
C(13)-H(26)	1.06	
C(15)-H(27)	1.04	
N(16)-H(28)	0.95	
C(17)-H(29)	1.03	
N(18)-H(30)	0.93	
C(12)-N(11)-H(20)	98	
C(12)-N(11)-H(21)	114	
C(12)-N(11)-H(22)	115	
H(20)-N(11)-H(21)	117	
H(20)-N(11)-H(22)	118	
H(21)-N(11)-H(22)	96	
N(11)-C(12)-H(23)	113	
N(11)-C(12)-H(24)	112	

Table 16 (Continued)

C(13)-C(12)-H(23)	113
C(13)-C(12)-H(24)	107
H(23)-C(12)-H(24)	100
C(12)-C(13)-H(25)	100
C(12)-C(13)-H(26)	106
C(14)-C(13)-H(25)	108
C(14)-C(13)-H(26)	113
H(25)-C(13)-H(26)	115
C(14)-C(15)-H(27)	128
N(16)-C(15)-H(27)	125
C(15)-N(16)-H(28)	126
C(17)-N(16)-H(28)	123
N(16)-C(17)-H(29)	127
N(18)-C(17)-H(29)	124
C(14)-N(18)-H(30)	131
C(17)-N(18)-H(30)	120

Phosphate groups

P(1)-O(3)	1.568
P(1)-O(4)	1.556
P(1)-O(5)	1.507
P(1)-O(6)	1.502
P(2)-O(7)	1.560
P(2)-O(8)	1.561
P(2)-O(9)	1.498
P(2)-O(10)	1.487

O(3)-H(33)	0.98
O(4)-H(36)	0.83
O(7)-H(34)	0.93
O(8)-H(35)	0.74

O(3)-P(1)-O(4)	107.7
O(3)-P(1)-O(5)	109.3
O(3)-P(1)-O(6)	106.1
O(4)-P(1)-O(5)	105.9
O(4)-P(1)-O(6)	112.0
O(5)-P(1)-O(6)	115.8
O(7)-P(2)-O(8)	106.3
O(7)-P(2)-O(9)	107.6
O(7)-P(2)-O(10)	111.5
O(8)-P(2)-O(9)	108.0
O(8)-P(2)-O(10)	108.0
O(9)-P(2)-O(10)	115.2

Table 16 (Continued)

```
P(1)-O(3)-H(33)         113
P(1)-O(4)-H(36)         114
P(2)-O(7)-H(34)         114
P(2)-O(8)-H(35)         109
```

Water molecule

```
O(19)-H(31)             0.91
O(19)-H(32)             1.02
H(31)-O(19)-H(32)       105
```

21, 20, 54, and 39 percent double bond character, respectively. This implies 66 percent double bond character for C(14)-C(15) and, at the same time a total contribution of tautomers I and II of about 60%. The preponderance of these tautomers is expected because they do not involve charge separation. The internal angles of the imidazole ring are equal to one another within the accuracy of the method.

The N(11)-C(12) bond length of 1.494 Å is slightly greater than the standard value of 1.479 Å, but agrees well with the α-carbon-amino-nitrogen bond lengths described for other amino acids; these range from 1.46 to 1.52 Å, the majority being close to 1.51 Å in length. The carbon-carbon bond lengths of the side chain have an average value of 1.494 Å which is significantly shorter than the standard paraffinic bond length of 1.541 Å.

The bond lengths and valency angles of the $H_2PO_4^-$ ions also are listed in Table 16. The mean P-O and P-OH distances of 1.561 and 1.499 Å (with a standard error of the mean of 0.005 Å) are in agreement with those observed in similar compounds (21-25). The bond lengths are also in good agreement with those predicted by π-bonding theories for ions of this type (23). Cruickshank (23) pointed out that the bond lengths for $H_2PO_4^-$ in a crystal are close to the average of those in PO_4^{-3} and those in $PO_2(OR)_2^-$ where R = alkyl. Presumably the deviation from the $PO_2(OR)_2^-$ bond length is due to hydrogen bonding of $H_2PO_4^-$ in the crystal. The predicted values for $H_2PO_4^-$ of 1.50 Å for P-O and 1.59 Å for P-OH are close to the observed values. Robinson (26) has used correlations between i.r. stretching frequencies and bond lengths to predict P-O and P-OH bond lengths of 1.48 and 1.58 Å for the $H_2PO_4^-$ ion.

The mean O-P-O angle of 115.5° differs significantly from the mean HO-P-OH angle of 107.0°. This deviation from a tetrahedral configuration would be expected on the basis of the electron-pair repulsion theory (27). The values are close to those observed for the $H_2PO_4^-$ ion in KH_2PO_4, namely, 115.4 and 105.5° respectively (21). The small differences among the various O-P-OH angles are possibly due to crystal packing.

The mean O-H bond length in the $H_2PO_4^-$ ion is 0.87 Å with a range of 0.74-0.98 Å (σ 0.15 Å). The difference between 0.87 Å and the 1.04 Å obtained for the same bond by means of neutron diffraction (21) is thought to be due to a nuclear displacement from the centre of the hydrogen electron cloud. The P-O-H angles with a mean of 112 ± 9° range from 109 to 114°.

The mean O-H bond length in the water molecule is 0.97 Å (σ 0.15 Å) and the H-O-H angle 105°, both as expected. The high temperature factors of the water molecule may be the result of weak hydrogen bonding or a slight variation in the water content.

The structure may be thought of as a leaning stack of histamine ions surrounded by a cylinder of $H_2PO_4^-$ ions and water molecules as shown in Figure 9. The significant features of the complex hydrogen bonding scheme which includes six O-H...O and five N-H...O bonds and involves every active hydrogen atom, are outlined in Figure 10 and Tables 17 and 18.

The observed bond angles and bond lengths of the hydrogen bonding system suggest that all the hydrogen bonds have been correctly assigned. In addition to those assigned, N(11) has a further two near oxygen
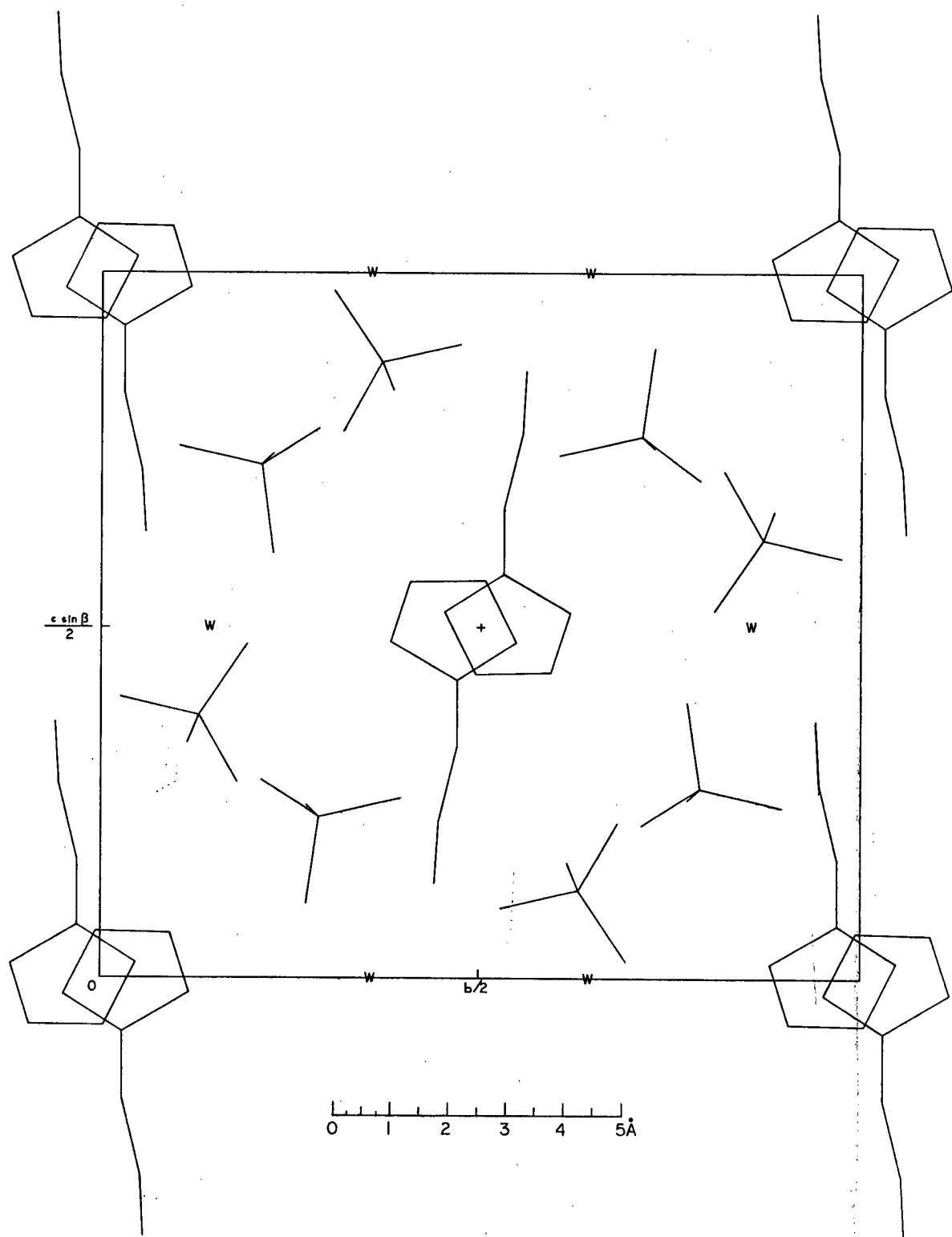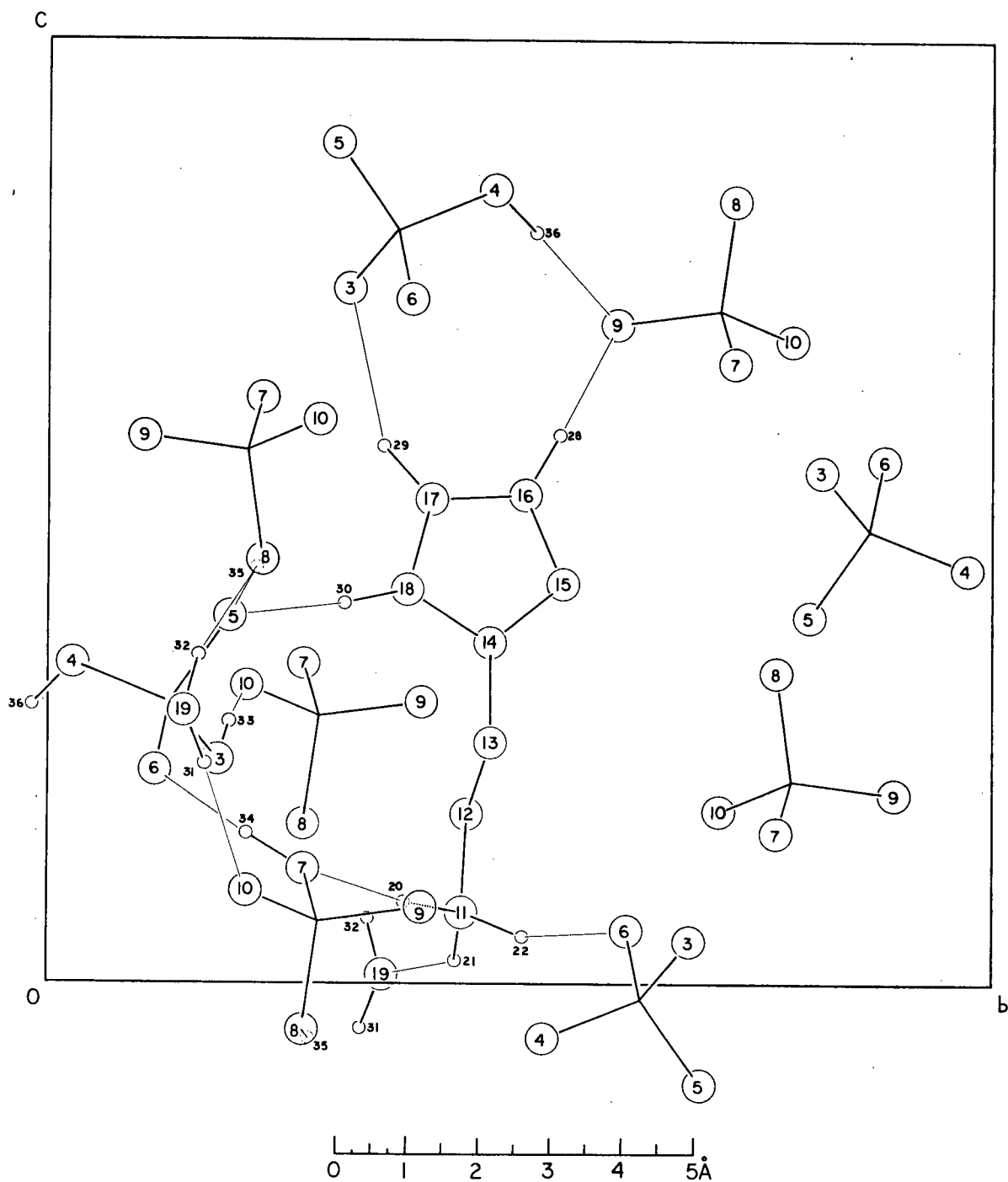
Figure 9.   Projection of structure along a.

Figure 10. Projection of the structure along a* showing the hydrogen bonding scheme. The short C-H...O contact is also shown.

Table 17

Distances (Å) and angles (degrees) in the hydrogen bonds X-H...O

(X = O or N)

Bond	X...O	X-H	H...O	H-X...O	Donor (X)	Acceptor
O(3)-H(33)...O(10^{I})[$\bar{1}$00]	2.55	0.98	1.59	9	OH	O
O(4)-H(36)...O(9^{IV})[101]	2.58	0.83	1.75	2	OH	O
O(7)-H(34)...O(6^{I})[000]	2.54	0.93	1.62	9	OH	O
O(8)-H(35)...O(5^{II})[00$\bar{1}$]	2.57	0.74	1.84	10	OH	O
O(19)-H(31)...O(10^{I})[000]	2.74	0.91	1.90	19	H_2O	O
O(19)-H(32)...O(8^{II})[000]	3.00	1.02	2.01	10	H_2O	OH
N(11)-H(21)...O(19^{II})[$\bar{1}$0$\bar{1}$]	2.77	0.94	2.02	31	NH_3^+	H_2O
N(11)-H(22)...O(6^{IV})[111]	2.86	0.98	1.96	19	NH_3^+	O
N(11)-H(20)...O(7^{I})[000]	3.18	1.06	2.13	6	NH_3^+	OH
N(16)-H(28)...O(9^{III})[111]	2.69	0.95	1.74	2	NH	O
N(18)-H(30)...O(5^{I})[000]	2.68	0.93	1.76	8	NH	O

Equivalent positions are shown by superior Roman numerals:

I	x	y	z
II	x	1/2-y	1/2+z
III	-x	-y	z
IV	-x	-1/2+y	-1/2-z

together with translation in a, b, and c indicated in square brackets.

Table 18

Environments of atoms involved in hydrogen bonding

Atoms involved	Angle in degrees
P(1)-O(3)...O(10)	121
P(1)-O(4)...O(9)	114
P(1)-O(5)...O(8)	123
P(1)-O(5)...N(18)	125
O(8)...O(5)...N(18)	96
P(1)-O(6)...O(7)	113
P(1)-O(6)...N(11)	128
O(7)...O(6)...N(11)	119
P(2)-O(7)...O(6)	123
P(2)-O(7)...N(11)	114
O(6)...O(7)...N(11)	123
P(2)-O(8)...O(5)	117
P(2)-O(8)...O(19)	121
O(5)...O(8)...O(19)	106
P(2)-O(9)...O(4)	119
P(2)-O(9)...N(16)	125
O(4)...O(9)...N(16)	108
P(2)-O(10)...O(3)	127
P(2)-O(10)...O(19)	127
O(3)...O(10)...O(19)	99
N(11)...O(19)...O(8)	117
N(11)...O(19)...O(10)	126
O(8)...O(19)...O(10)	115
C(15)-N(16)...O(9)	128
C(17)-N(16)...O(9)	122
C(15)-N(16)-C(17)	109
C(14)-N(18)...O(5)	133
C(17)-N(18)...O(5)	117
C(14)-N(18)-C(17)	109
C(12)-N(11)...O(6)	106
C(12)-N(11)...O(7)	96
C(12)-N(11)...O(19)	89
O(6)...N(11)...O(7)	100
O(6)...N(11)...O(19)	143
O(7)...N(11)...O(19)	112

neighbours: O(4) at 3.13 Å and O(5) at 3.11 Å. Since the corresponding

N-H...O angles are 156 and 148° respectively, they are not likely to

be bonded to N(11). Moreover, the position of H(20) favors the O(7)

bond.

As indicated in Figure 10, the water molecule is linked via two

O-H...O hydrogen bonds to the phosphate network. The water molecule

accepts one hydrogen from the terminal nitrogen of histamine. The four

O-H...O bonds between the phosphate ions are typical of the distances

reported for inorganic acids (18). The hydrogen bonds formed by the

water as a donor are 2.74 and 3.00 Å, also within the usual range (18).

The histamine ion acting as a donor forms a total of five N-H...O

bonds which range from 2.66 to 3.18 Å in length and involve four

different phosphate ions and one water molecule (Figure 10). Except

for the N(18)-H(30)...O(5) bond length of 3.18 Å, the bonds are in

the usual range (24). The geometry of this long bond is otherwise quite

acceptable.

The N(11) atom is roughly in a tetrahedral configuration although

the O(6)...N(11)...O(19) angle of 143° (Table 18) does deviate appreciably

from the tetrahedral value. The hydrogens of N(11) approach a tetra-

hedral arrangement much closer (Table 16). Oxygens (3) and (4) take part

in only one hydrogen bond each. All other oxygen atoms participate in

two hydrogen bonds. The arrangement of covalent and hydrogen bonds

around the oxygen atoms approximates planarity with the sum of the sets

of three angles ranging between 344 and 360°. The hydrogen bonds show

the usual deviation (28) from 180°, of up to about 30° as indicated in

Table 17.

There are only two other short intermolecular distances in the

structure. One is an N(16)...N(16) distance of 3.10 Å across the centre

of symmetry; the contact is between two molecules whose planes are

parallel, and is slightly longer than the sum of the van der Waals radii

(3.0 Å). The second contact is a C(17)-H(29)...O(3) interaction

(Figure 10). The C...O distance is 3.14 (σ 0.017) Å, the H...O

distance is 2.22 (σ 0.15) Å, and the H-C...O angle 22°. Donohue (28),

who has described similar contacts, concluded that they did not

represent hydrogen bonds in the same sense as O-H...O or N-H...O bonds.

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