that of a bimolecular substitution reaction in which the attacking group approaches the reactive center from the side not occupied by another substituent. This interpretation is further supported by the structure analysis of *o*-nitrobenzaldehyde (Fig. 6) (Coppens & Schmidt, 1964; Coppens, 1964) in which the nonplanarity of the molecule provides a similar arrangement of the reactive centers C–H and N–O.

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References

BACON, G. E. & CURRY, N. A. (1956). *Proc. Roy. Soc.* A, **235**, 552.
BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
BOLTON, W. (1963). *Acta Cryst.* **16**, 950.
COHEN, M. D. & SCHMIDT, G. M. J. (1964). *J. Chem. Soc.* p. 1996.
COPPENS, P. (1962). *J. Chem. Phys.* **36**, 2523.
COPPENS, P. (1964). *Acta Cryst.* **17**, 573.
COPPENS, P. & SCHMIDT, G. M. J. (1964). *Acta Cryst.* **17**, 222.
COPPENS, P. & SCHMIDT, G. M. J. (1965). *Acta Cryst.* **18**, 62.
COX, E. G., CRUICKSHANK, D. W. J. & SMITH, J. A. S. (1958). *Proc. Roy. Soc.* A, **247**, 1.
CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 896.
FRITZSCHE, J. (1859). *Liebigs Ann.* **110**, 157.
FURNAS, T. C. Jr. (1957). *Single Crystal Orienter Manual.* Milwaukee: General Electric Co.
HAMILTON, W. C. (1957). *Acta Cryst.* **10**, 629.
HIRSHFELD, F. L. (1964). *Israel J. Chem.* **2**, 87.
HIRSHFELD, F. L., SANDLER, S. & SCHMIDT, G. M. J. (1963). *J. Chem. Soc.* p. 2108.
HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
KITAIGORODSKII, A. I. (1957). *Organic Chemical Crystallography.* English translation by Consultants Bureau, New York.
MCWEENY, R. (1952). *Acta Cryst.* **5**, 463.
MOE, K. M. (1963). *Acta Cryst.* **16**, A 58.
NAKAMOTO, K., MARGOSHES, M.M. & RUNDLE, R. E. (1955). *J. Amer. Chem. Soc.* **77**, 6480 .
ROBERTSON, J. M. (1936). *Proc. Roy. Soc.* A, **157**, 79.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
SUTTON, L. E. (1958). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* London: The Chemical Society.
TOUSSAINT, J. (1954). *Bull. Soc. Sci. Liège*, **23**, 24.
TRUEBLOOD, K. N., GOLDISH, E. & DONOHUE, J. (1961). *Acta Cryst.* **14**, 1009.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1965). **18**, 663

The Structure of α-Chlorohemin*

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Chlorohemin, $C_{34}H_{32}N_4O_4FeCl$, forms soft, lath-shaped crystals of the α modification, space group $P1$ or $P\bar{1}$, $Z=2$, $a=11{\cdot}49$, $b=14{\cdot}10$, $c=10{\cdot}85$ Å, $\alpha=98{\cdot}56°$, $\beta=108{\cdot}49°$, $\gamma=107{\cdot}65°$. Three-dimensional Mo $K\alpha$ data were collected with a spectrogoniometer. The iron and chlorine atoms, located through Patterson syntheses and superposition functions, were used to initiate determination of the structure largely through F_o-F_c syntheses. Full-matrix least-squares refinement and concurrent F_o-F_c refinement reduced the value of R to 0.095 for the 1566 observed reflections.

The iron atom of chlorohemin lies out of the plane of the four nitrogen atoms toward the chlorine atom. While each of the pyrrole residues is planar, the porphyrin ring is slightly puckered. The two vinyl residues per molecule were not located unambiguously; they are disordered in pairs, or noncentrosymmetrically arranged, in the unit cell.

Introduction

Metallo-porphyrins are among the most ancient, universal, and extensively studied prosthetic groups of proteins (Lemberg & Legge, 1949). Nonetheless, attempts to determine mechanisms of actions of hemoproteins have been frustrated by lack of knowledge of configurational details of the porphyrins and bonding states of the iron atom (Falk, Lemberg & Morton, 1961). It was accordingly decided to undertake the determination of several iron porphyrin structures in this laboratory. Chlorohemin was chosen as the first of these because of the extensive chemical studies upon it and because of its biological importance as an iron protoporphyrin IX compound.

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Crystal preparation

Among several reported crystal forms, only α or Teichmann crystals have been clearly shown to be composed of chlorohemin (Lemberg & Legge, 1949; pp. 167–8). Chlorohemin obtained either from commercial sources, or from beef blood by the method of Fischer (1941, p. 53) was recrystallized by a modification of the method of Fischer & Orth (1937):

0·2 g of chlorohemin in 1·0 ml of pyridine and 1·4 ml of tetrachloroethane were mixed with 14 ml of glacial acetic acid and held at 120 °C in a test tube. A length of dialysis tubing, perforated with pinholes, coated with mineral oil, and filled with a concentrated aqueous solution of sodium chloride, was lowered into the test tube. α-Chlorohemin crystals, maximum size $2 \times 0{\cdot}5 \times 0{\cdot}05$ mm, formed on the surface of the tubing. α-Bromohemin crystals were prepared by Dr. W. E. Love by layering a chloroform solution of the pyridine complex under glacial acetic acid saturated with sodium bromide.

Data collection

Lattice parameters for α-chlorohemin were measured with a spectrogoniometer. Those for α-bromohemin were taken from precession photographs. The two sets of parameters are given in Table 1 with estimated accuracies. Chlorohemin crystals slowly sank in a carbon tetrachloride–chloroform mixture (density 1·38 g. cm^{-3}) and floated in trichloroethylene (density 1·46 g. cm^{-3}). The calculated density of α-chlorohemin, assuming two molecules per unit cell and no other constituents, is 1·415 g. cm^{-3}. The space group is $P1$ or $P\bar{1}$ (see below) and $Z=2$.

Table 1. *Lattice parameters and estimated maximum errors for α-chlorohemin and α-bromohemin*

	α-chlorohemin	α-bromohemin
a	11·494 ± 0·02Å	11·55 ± 0·06Å
b	14·097 ± 0·02	14·16 ± 0·06
c	10·854 ± 0·02	10·82 ± 0·06
α	98·56 ± 0·04°	98·53 ± 0·20°
β	108·49 ± 0·04	107·67 ± 0·20
γ	107·65 ± 0·04	107·68 ± 0·20
Volume	1530Å^3	1550Å^3

Two projections of chlorohemin were recorded with a Weissenberg camera and Mo $K\alpha$ radiation. In the second plane recorded, $0kl$, agreement of intensities of equivalent reflections was unsatisfactory. The first recorded plane, $hk0$, was used in initial stages of locating the iron and chlorine atoms.

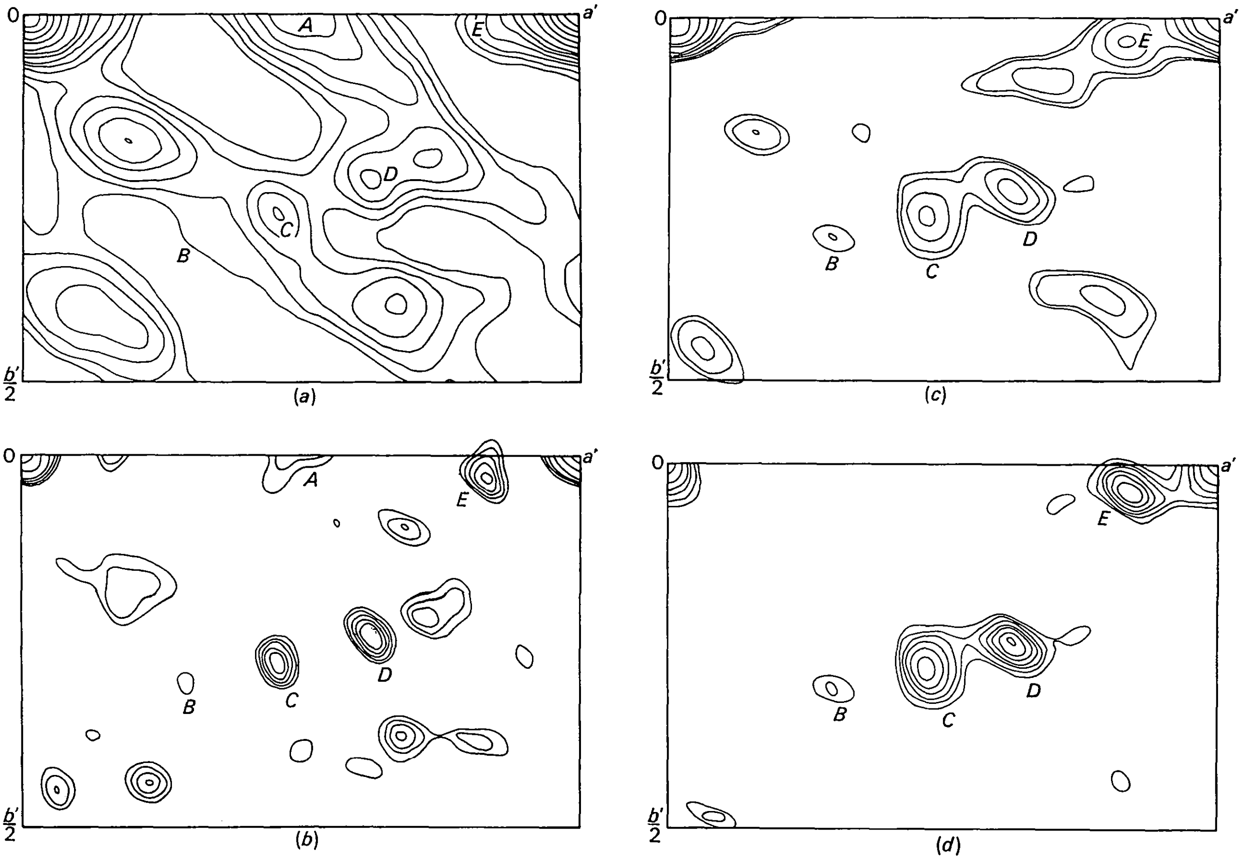

Fig. 1. $hk0$ Patterson projections and minimum functions. See text for details. The projections are contoured at arbitrary levels directly from computer output. Axes a' and b' lie only approximately in the directions of a and b.

Three-dimensional data were collected from one crystal with a General Electric XRD5 spectrometer equipped with goniostat, Mo tube, scintillation counter, and Zr–Sr balanced filters. The optics were modified to accommodate the broad reflections, up to 1·0° θ, encountered. All reflections within $\theta = 15·6°$, and several hundred of the infrequent measurable reflections beyond this limit, were recorded by the $\theta,2\theta$ scan technique with balanced filters. 1566 independent reflections were observed, of which 230 were below the limit of reliable measurement. Lorentz-polarization corrections and later absorption corrections (Burnham, 1962) were applied. The maximum absorption was 24%. No evidence of extinction or crystal deterioration was found.

The absolute scale factor and overall temperature factor (3·74 Å^2) were estimated by Wilson's method. A statistical analysis (Howells, Phillips & Rogers, 1950) strongly indicated the space group to be $P\bar{1}$ rather than $P1$, but small deviations from centrosymmetry cannot be ruled out (see below).

Scattering factors were taken from the following sources: H, McWeeny (1951); C, N, O, and Cl$^-$, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal, (1955); Fe^{3+}, Watson & Freeman (1961). Real parts of the dispersion corrections were applied to the iron and chlorine factors.

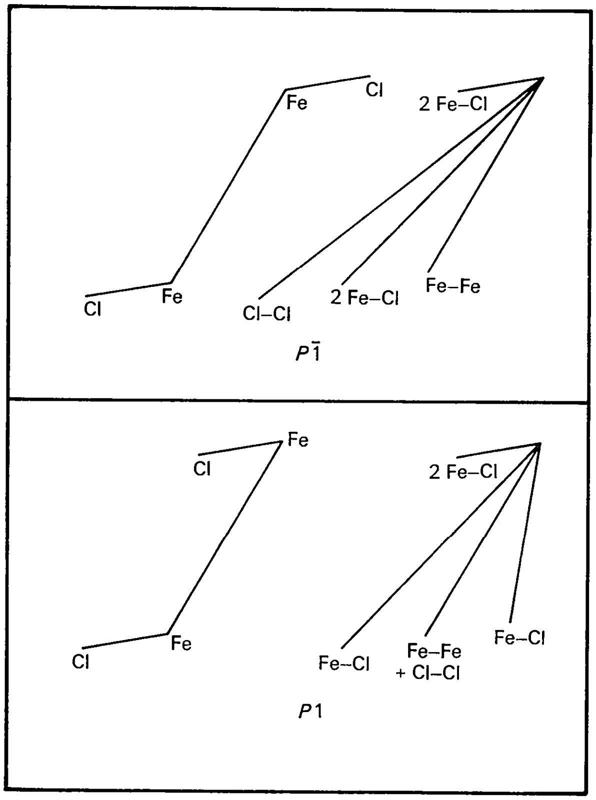

Fig. 2. Centric and acentric configurations of iron and chlorine atoms are illustrated diagrammatically (left) with the resultant Patterson peaks (right).

Structure determination

The unsharpened $hk0$ Patterson projection shows a pseudo-repeat along a' at $a'/2$ (Fig. 1(*a*)). The same projection, sharpened by the function of Schomaker & Shoemaker (Lipson & Cochran, 1957, p. 173) resembles the "partial Patterson" projection (Buerger, 1959, p. 321) based on the pseudo-repeat along a' [Fig. 1 (*b*), (*c*)].

On these projections, only one peak occurs at about 2Å from the origin. If this is an iron-chlorine peak, the projections of the two iron-chlorine bonds in the two molecules of the unit cell must be parallel. Then there are two possible arrangements of the iron and chlorine atoms (Fig. 2), which give rise to sets of Patterson peaks which have the same geometrical arrangement but quite different weightings. The centrosymmetric arrangement of iron and chlorine atoms was indicated. This choice was supported by the minimum function (Buerger, 1959) derived from the unsharpened Patterson projection by a shift of peak C to the origin [Fig. 1(*d*)]. Further minimum functions based on the chosen arrangement could not be interpreted at the time.

Henceforth only the three-dimensional data were used. The three-dimensional Patterson function is dominated by sheets of high density roughly parallel to $(3\bar{2}\bar{1})$. A minimum function in the high-density sheet through the origin, based on the approximate fourfold symmetry implied by the chemical structure (Fischer & Orth, 1937), permitted estimation of the angular orientation of the porphyrin ring to within five degrees of the final position. This information, though possibly sufficient to yield a solution of the structure, was used only as a guide.

The Patterson function also contains an iron-chlorine peak near the origin, and two prominent peaks corresponding in x and y coordinates to the peaks in the $hk0$ projection identified with iron–iron and iron–chlorine vectors. The difference in z coordinates of the two peaks equals the z coordinate of the short iron–chlorine vector, as required by the identities assigned the peaks.

However, the peak identified with the iron–iron vector lies well to one side of a high-density sheet in the Patterson function, while the supposed iron–chlorine peak (C, Fig. 1) lies within a high-density sheet. Since, in all similar structures, the metal atom had been found to lie in the mean plane of the macrocyclic ring, the latter peak was reinterpreted as the iron–iron peak. On this basis, a "heavy atom" F_o–F_c synthesis based on iron and chlorine signs was computed; choice of the space group as $P\bar{1}$ is unavoidable. A recognizable fourfold pattern appeared around the supposed iron position. However, it was clear that whatever the space group or detailed positions of the atoms might be, the two molecules of the cell would interpenetrate extensively, near the center of the unit cell.

With the originally chosen positions of the iron and chlorine atoms, *i.e.* with the iron atom out of the plane of the porphyrin ring, a heavy atom F_o–F_c synthesis was again computed, and again a crude porphyrin pattern appeared, but now the molecules did not interpenetrate. The iron atom lay out of the porphyrin plane by about 0·4 Å.

Input to the next F_o–F_c synthesis included all the porphyrin ring atoms and the eight innermost atoms of the side groups. The synthesis displayed the propionate groups clearly; the two carboxyl groups of one molecule were seen to be hydrogen-bonded to those of a molecule in an adjacent unit cell. *Four* low peaks per molecule appeared at possible positions for outer atoms of vinyl groups attached to atoms *A*2, *A*3, *D*2, and *D*3 of the porphyrin ring (Fig. 3). Since there are only two vinyl groups per molecule, no use of the four peaks was made.

After several unsuccessful attempts to enforce coplanarity of the iron atom and porphyrin ring by moving either or both, refinement by F_o–F_c syntheses continued with space group assumed $P\bar{1}$ and one isotropic temperature factor per element, until *R* fell to 0·195. The four low peaks persisted. The oxygen atoms were seen to be extended normal to the plane of hydrogen bonding.

Inclusion of fourteen hydrogen atoms per molecule at calculated positions reduced the value of *R* to 0·179. Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1961) was then undertaken; all reflections were given equal weight throughout the investigation. Upon two refinement cycles with isotropic temperature factors, the value of *R* fell to 0·153, and then to 0·125 after the oxygen atoms were permitted anisotropic temperature factors. The four low peaks persisted, at about half the height characteristic of carbon atoms. Elementary analyses confirmed the presence of the expected 34 carbon atoms per molecule (C: calc. 62·63%; found 62·27, 62·39%. H: calc. 4·95%; found 4·77, 4·92%).

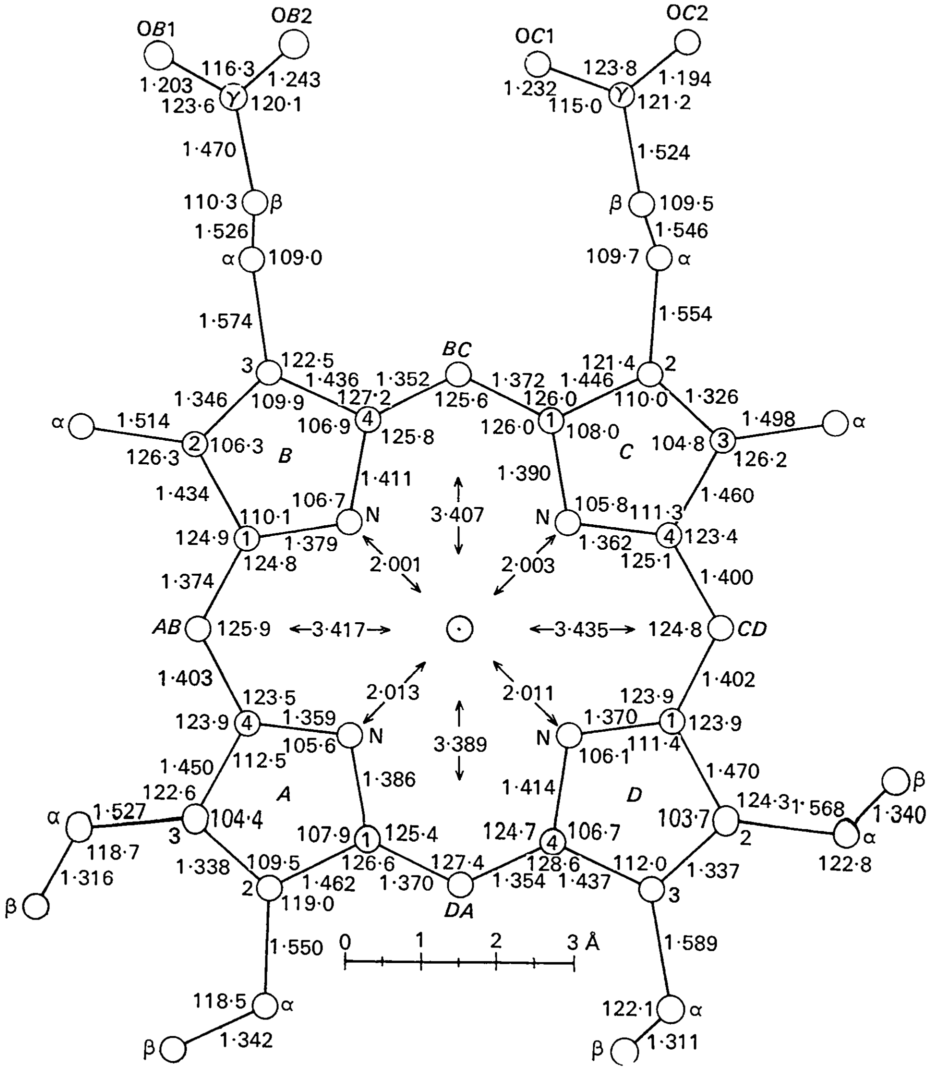

Fig. 3. Projection of the molecule onto the plane of the nitrogen atoms. The iron and chlorine atoms, not shown, lie below the plane of the figure. *Either* atoms *A*2*β* and *D*2*β*, *or* *A*3*β* and *D*3*β*, are present in a given molecule. Values of bond lengths and angles are given to four digits for purposes of record only.

Table 2. *Observed and calculated structure factors*

K	L	|FOBS|	FCALC
H =	0		
0	0		650.8
0	1	47.2	-43.1
0	2	63.4	-60.9
0	3	38.7	40.
0	4	22.8	-24.5
0	5	7.4	7.7
0	6	19.9	23.2
0	7	18.3	-21.4
1	-7	11.4	10.1
1	-6	17.6	-16.7
1	-5	56.1	53.7
1	-4	2.3	1.4
1	-3	78.0	-70.6
1	-2	56.5	42.2
1	-1	38.4	-39.8
1	0	74.8	-87.
1	1	29.5	30.3
1	2	55.7	-56.9
1	3	43.2	-43.9
1	4	14.3	15.1
1	5	16.2	-15.9
1	6	5.5	-9.8
1	7	11.9	11.4
2	-7	8.0	5.
2	-6	25.7	26.2
2	-5	67.5	-61.5
2	-4	52.7	47.6
2	-3	9.8	-8.9
2	-2	62.8	-57.3
2	-1	1.4	1.7
2	0	9.3	-19.6
2	1	57.4	-56.4
2	2	59.4	60.7
2	3	17.2	-15.6
2	4	20.0	19.6
2	5	17.6	16.8
2	6	10.5	-12.7
3	-7	33.9	-34.8
3	-6	2.9	-2.3
3	-5	26.4	26.5
3	-4	82.7	-72.6
3	-3	35.1	36.8
3	-2	21.1	21.2
3	-1	17.7	18.5
3	0	68.4	68.6
3	1	50.2	-49.8
3	2	59.2	-55.1
3	3	19.8	23.9
3	4	14.5	-12.7
3	5	38.7	-39.5
3	6	21.6	21.4
4	-7	37.3	35.4
4	-6	3.1	1.9
4	-5	3.7	-3.5
4	-4	67.9	63.6
4	-3	59.9	-54.8
4	-2	5.6	6.1
4	-1	34.1	38.
4	0	46.9	-46.
4	1	40.3	37.6
4	2	32.3	34.1
4	3	53.6	-54.
4	4	22.0	22.5
4	5	3.1	5.9
4	6	9.1	-7.5
5	-7	18.4	-18.5
5	-6	20.8	20.9
5	-5	39.9	-36.3
5	-4	5.7	-6.6
5	-3	13.5	-7.1
5	-2	120.0	-116.3
5	-1	30.9	32.
5	0	91.3	93.2
5	1	56.0	-56.6
5	2	19.2	18.4
5	3	22.4	21.3
5	4	15.3	-16.2
5	5	12.5	13.5
6	-7	21.3	-18.2
6	-6	6.1	-12.3
6	-5	52.9	55.2
6	-4	31.1	-31.6
6	-3	25.6	23.4
6	-2	27.7	-24.6
6	-1	28.2	-29.5
6	0	21.9	25.6
6	1	30.9	30.1
6	2	24.5	-23.2
6	3	5.1	4.5
6	4	3.2	4.1
7	-7	18.4	19.8
7	-6	3.3	-5.5
7	-5	8.8	6.5
7	-4	34.5	37.2
7	-3	29.8	-30.5
7	-2	17.7	13.3
7	-1	42.5	42.3
7	0	29.9	-33.4
7	1	5.7	8.4
7	2	6.1	-4.8
7	3	16.6	-18.3
8	-6	10.8	12.1
8	-5	6.1	-6.7
8	-4	33.2	-35.
8	-3	31.0	31.
8	-2	14.2	-13.8
8	-1	17.6	16.7
8	0	30.0	32.5
8	1	25.9	-26.7
8	2	10.7	-10.7
9	-5	11.1	13.8
9	-4	7.9	5.8
9	-3	43.3	-43.5
9	-2	18.7	16.8
9	-1	11.7	-9.8
9	0	21.5	-22.6
9	1	21.1	21.3
10	-3	3.4	2.8
10	-2	18.4	-25.
10	-1	11.1	14.8
10	0	4.3	-9.8
H =	1		
-10	-2	20.7	-21.6
-10	-1	19.5	20.7
-10	0	10.5	8.8
-10	1	3.3	-1.2
-10	2	10.1	6.6
-10	3	17.9	16.5
-10	4	20.7	-20.5
-9	-2	14.3	15.4
-9	-1	15.6	-19.5
-9	0	3.1	0.3
-9	1	21.7	24.8
-9	2	31.7	-28.
-9	3	5.7	2.9
-9	4	18.6	17.7
-9	5	17.5	-19.7
-9	6	18.5	-15.6
-8	-3	3.3	-4.9
-8	-2	3.1	-4.8
-8	-1	10.1	12.2
-8	0	30.9	-31.8
-8	1	2.9	-1.2
-8	2	19.2	19.3
-8	3	27.9	-27.3
-8	4	21.9	-19.4
-8	5	19.4	18.2
-8	6	10.5	-8.8
-7	-4	15.5	-13.4
-7	-3	3.1	1.4
-7	-2	2.9	2.6
-7	-1	8.4	-9.1
-7	0	49.6	45.6
-7	1	21.6	19.8
-7	2	32.4	-31.4
-7	3	10.1	10.5
-7	4	16.9	-14.
-7	5	14.1	-12.9
-7	6	43.3	41.2
-7	7	23.6	-21.8
-7	8	11.0	-12.3
-7	9	24.1	20.7
-6	-5	3.3	2.3
-6	-4	4.8	-6.1
-6	-3	21.9	-19.7
-6	-2	10.2	10.4
-6	-1	10.4	-11.
-6	0	9.1	5.8
-6	1	7.7	8.9
-6	2	16.4	-14.1
-6	3	30.1	-32.6
-6	4	52.1	48.6
-6	5	3.2	-1.6
-6	6	9.9	-12.8
-6	7	45.9	42.2
-5	-5	5.0	0.4
-5	-4	12.2	13.4
-5	-3	2.7	-2.8
-5	-2	45.4	-45.
-5	-1	11.5	5.2
-5	0	31.6	31.1
-5	1	11.3	-11.5
-5	2	18.2	-13.
-5	3	20.3	19.3
-5	4	73.0	-66.7
-5	5	3.0	1.1
-5	6	22.4	20.1
-5	7	26.0	-26.3
-4	-6	7.4	4.5
-4	-5	7.7	8.8
-4	-4	10.6	-4.8
-4	-3	17.0	-15.2
-4	-2	26.2	27.2
-4	-1	13.5	-1.1
-4	0	2.0	-3.9
-4	1	56.6	55.8
-4	2	44.6	-40.5
-4	3	60.9	49.3
-4	4	24.9	24.7
-4	5	43.4	-43.2
-4	6	5.9	8.2
-4	7	9.1	8.6
-3	-7	17.1	19.6
-3	-6	24.0	-22.5
-3	-5	21.7	-22.4
-3	-4	13.6	-11.5
-3	-3	26.2	23.7
-3	-2	2.0	5.
-3	-1	32.1	23.4
-3	0	7.0	8.4
-3	1	22.0	-22.9
-3	2	54.5	48.8
-3	3	64.5	-60.6
-3	4	34.5	34.5
-3	5	33.5	33.9
-3	6	41.9	-43.8
-3	7	14.1	14.9
-2	-7	3.3	-5.1
-2	-6	32.6	31.
-2	-5	32.8	34.9
-2	-4	13.5	-11.1
-2	-3	26.0	26.2
-2	-2	1.8	11.8
-2	-1	13.8	-22.9
-2	0	83.6	71.6
-2	1	24.4	-13.6
-2	2	23.3	-17.7
-2	3	64.5	57.9
-2	4	73.2	-72.8
-2	5	25.7	25.5
-2	6	24.3	24.5
-2	7	17.7	-16.7
-1	-7	3.2	-1.2
-1	-6	14.0	-15.1
-1	-5	13.2	-10.8
-1	-4	25.4	31.
-1	-3	24.3	-22.2
-1	-2	91.2	-91.1
-1	-1	109.4	-102.1
-1	0	7.4	17.6
-1	1	38.6	42.1
-1	2	60.2	-57.8
-1	3	27.3	-24.8
-1	4	5.2	0.3
-1	5	43.0	-43.5
-1	6	3.0	4.2
-1	7	20.9	24.5
0	-7	5.6	-8.8
0	-6	4.5	7.6
0	-5	16.7	-16.3
0	-4	12.5	11.9
0	-3	39.8	44.2
0	-2	74.1	-68.
0	-1	115.5	115.8
0	0	52.0	-46.8
0	1	35.8	38.2
0	2	3.2	3.9
0	3	40.3	-35.5
0	4	13.1	-13.2
0	5	37.4	38.4
0	6	31.7	-32.1
0	7	3.3	0.6
1	-7	16.9	-16.7
1	-6	17.6	19.8
1	-5	18.9	18.3
1	-4	62.0	-58.3
1	-3	28.6	-21.7
1	-2	29.5	29.5
1	-1	44.9	-50.1
1	0	51.9	48.4
1	1	11.8	18.5
1	2	37.8	-37.8
1	3	91.2	88.6
1	4	2.6	-2.8
1	5	30.1	-28.5
1	6	41.6	47.5
1	7	21.5	-19.2
1	8	3.6	1.1
2	-8	3.3	-4.8
2	-7	17.6	20.4
2	-6	35.5	-32.
2	-5	21.6	22.5
2	-4	49.8	47.5
2	-3	53.4	-53.2
2	-2	13.8	6.2
2	-1	45.7	43.2
2	0	57.9	-59.3
2	1	22.5	22.7
2	2	6.6	-7.8
2	3	11.9	9.4
2	4	28.8	31.
2	5	17.1	-16.6
2	6	26.8	-29.3
2	7	43.8	48.8
2	8	9.1	-8.4
3	-8	20.8	-21.2
3	-7	7.0	-6.9
3	-6	30.1	26.7
3	-5	31.2	-31.2
3	-4	24.2	21.9
3	-3	38.1	40.7
3	-2	53.6	-56.5
3	-1	25.6	20.6
3	0	46.6	41.8
3	1	83.9	-78.
3	2	36.9	31.9
3	3	2.6	5.
3	4	28.4	-26.9
3	5	34.5	34.9
3	6	3.3	-6.9
3	7	18.6	-21.6
3	8	3.8	5.1
4	-8	27.8	24.6
4	-7	9.7	-10.
4	-6	14.7	-16.1
4	-5	55.2	53.7
4	-4	26.2	-29.5
4	-3	13.4	-8.6
4	-2	46.4	43.8
4	-1	37.2	-37.4
4	0	47.0	43.
4	1	44.1	41.3
4	2	65.1	-64.1
4	3	30.6	31.1
4	4	11.7	-12.8
4	5	24.2	-27.1
5	-8	19.3	-17.8
5	-7	27.3	24.5
5	-6	9.7	-8.8
5	-5	24.7	-23.3
5	-4	51.3	50.8
5	-3	24.5	22.7
5	-2	37.5	-38.8
5	-1	16.9	-14.8
5	0	59.5	-62.1
5	1	10.5	9.5
5	2	40.8	39.4
5	3	30.3	-34.9
5	4	7.5	9.8
6	-10	12.6	-12.2
6	-9	16.2	12.7
6	-8	3.6	3.6
6	-7	35.4	-31.8
6	-6	33.7	35.9
6	-5	2.9	1.8
6	-4	26.3	-26.3
6	-3	2.6	5.1
6	-2	8.7	-12.7
6	-1	36.3	-35.8
6	0	64.3	64.8
6	1	29.2	-30.8
6	2	12.8	13.6
6	3	42.3	42.9
6	4	10.1	-9.1
7	-9	13.0	-17.9
7	-8	3.7	-4.2
7	-7	3.4	4.9
7	-6	25.8	-23.7
7	-5	22.7	26.4
7	-4	2.9	-0.2
7	-3	38.4	-35.3
7	-2	42.2	47.3
7	-1	10.9	-15.2
7	0	13.6	-16.8
7	1	3.0	-5.1
7	2	22.5	-24.7
7	3	3.3	-2.5
8	-6	9.5	10.7
8	-5	29.6	-27.6
8	-4	50.1	49.9
8	-3	3.0	-5.1
8	-2	29.7	-30.7
8	-1	27.6	28.8
8	0	3.1	-2.7
8	1	23.2	-25.
8	2	33.3	31.8
8	3	10.5	-7.9
9	-5	6.1	7.6
9	-4	49.0	-48.4
9	-3	25.7	25.7
9	-2	3.2	-3.7
9	-1	14.2	-9.9
9	0	20.2	22.
9	1	3.4	-1.4
9	2	3.5	4.3
9	3	6.7	11.1
10	-5	16.7	12.1
10	-4	37.3	36.
10	-3	3.4	-3.3
10	-2	10.4	9.5
10	-1	14.4	-12.3
10	0	0.0	-2.7
H =	2		
-10	-2	13.6	16.
-10	-1	3.4	-1.7
-10	0	15.5	-16.6
-10	1	5.9	10.2
-10	2	6.0	9.2
-10	3	25.1	-23.7
-10	4	14.3	11.1
-9	-2	3.3	2.8
-9	-1	3.2	1.3
-9	0	3.1	2.4
-9	1	23.1	-23.2
-9	2	19.0	20.6
-9	3	5.3	8.7
-9	4	7.5	-8.
-9	5	3.5	-6.3
-8	-4	23.9	-23.
-8	-3	13.2	-15.
-8	-2	16.9	16.3
-8	-1	35.6	-34.3
-8	0	2.9	-1.3
-8	1	2.9	5.4
-8	2	37.2	35.4
-8	3	3.1	-0.5
-8	4	3.2	-1.6
-8	5	16.8	-14.3
-8	6	11.7	10.2
-7	-4	21.7	25.9
-7	-3	7.6	-7.
-7	-2	21.3	-23.8
-7	-1	40.4	38.3
-7	0	35.4	31.5
-7	1	4.8	2.2
-7	2	17.8	-10.5
-7	3	7.0	-5.2
-7	4	13.2	-15.3
-7	5	18.4	15.7
-7	6	11.7	-12.5
-6	-5	12.3	15.8
-6	-4	23.6	-22.1
-6	-3	43.5	43.5
-6	-2	11.9	-14.8
-6	-1	44.1	-40.7
-6	0	2.5	-0.7
-6	1	12.9	-11.
-6	2	2.7	1.
-6	3	34.7	34.
-6	4	16.0	-12.7
-6	5	23.5	-20.2
-6	6	18.6	18.2
-5	-6	23.5	-24.2
-5	-5	12.7	12.3
-5	-4	5.0	5.9
-5	-3	16.1	-12.8
-5	-2	34.7	30.9
-5	-1	23.7	-20.3
-5	0	23.5	-23.1
-5	1	17.2	16.9
-5	2	10.2	7.8
-5	3	31.3	-27.4
-5	4	14.2	19.6
-5	5	3.0	0.1
-5	6	23.8	-26.2
-5	7	19.0	21.5
-4	-8	29.9	-35.5
-4	-7	13.4	18.5
-4	-6	14.5	15.7
-4	-5	10.7	-15.7
-4	-4	20.0	-18.3
-4	-3	31.2	32.6
-4	-2	5.7	2.5
-4	-1	13.9	-9.7
-4	0	2.2	-8.2
-4	1	2.2	-0.7
-4	2	2.3	5.1
-4	3	22.1	22.3
-4	4	24.8	-22.7
-4	5	2.9	-1.5
-4	6	5.6	5.4
-4	7	12.2	-10.6
-4	8	4.6	-9.3
-3	-7	26.7	-27.6
-3	-6	7.7	5.8
-3	-5	5.3	-5.3
-3	-4	28.4	-23.2
-3	-3	5.9	-8.1
-3	-2	4.1	-7.4
-3	-1	18.0	-10.1
-3	0	122.3	-112.3
-3	1	37.7	35.6
-3	2	51.4	50.1
-3	3	12.8	8.6
-3	4	17.5	20.4
-3	5	35.8	-37.4
-3	6	3.1	4.2
-2	-7	15.0	21.1
-2	-6	12.0	-14.3
-2	-5	7.4	-12.3
-2	-4	28.1	33.8
-2	-3	35.4	30.1
-2	-2	94.4	-85.5
-2	-1	65.0	60.4
-2	0	70.2	-66.7
-2	1	9.7	-11.
-2	2	38.8	40.4
-2	3	2.3	-2.9
-2	4	27.1	-25.9
-2	5	26.6	24.3
-2	6	3.1	-1.2
-2	7	3.4	6.9
-2	8	10.5	11.6
-1	-7	5.6	-5.8
-1	-6	17.2	18.5
-1	-5	28.1	21.8
-1	-4	7.3	-2.8
-1	-3	50.8	44.4
-1	-2	1.8	0.3
-1	-1	69.4	-73.6
-1	0	113.2	112.
-1	1	103.0	101.3
-1	2	36.4	-34.
-1	3	27.4	26.6
-1	4	8.1	7.5
-1	5	11.6	-13.3
-1	6	26.1	26.2
0	-8	3.3	2.5
0	-7	3.1	5.3
0	-6	17.0	-19.1
0	-5	25.1	22.4
0	-4	2.3	-2.4
0	-3	26.4	22.
0	-2	22.0	18.8
0	-1	43.7	-43.9
0	0	39.1	-35.2
0	1	25.2	17.3
0	2	5.6	5.8
0	3	16.4	-17.2
0	4	6.0	-3.9
0	5	29.0	-28.6
0	6	16.9	-17.4
0	7	3.4	3.
1	-8	6.4	-6.2
1	-7	11.2	15.5
1	-6	10.6	-9.9
1	-5	32.9	-34.
1	-4	12.5	9.
1	-3	34.4	31.4
1	-2	6.5	0.6
1	-1	41.1	-49.3
1	0	18.8	23.5
1	1	59.4	-56.1
1	2	7.1	-9.4
1	3	44.8	43.9
1	4	13.9	-11.8
1	5	40.3	37.6
1	6	11.0	-20.
1	7	17.5	-18.2
1	8	7.0	6.1
2	-8	12.3	10.8
2	-7	3.5	1.4
2	-6	2.8	-5.4
2	-5	20.4	17.4
2	-4	27.9	-25.1
2	-3	2.1	-4.8
2	-2	1.9	6.2
2	-1	44.9	-42.
2	0	34.7	-27.8
2	1	30.6	31.
2	2	28.1	-31.2
2	3	17.6	16.2
2	4	9.8	9.6
2	5	35.7	-34.9
2	6	30.3	34.9
2	7	3.6	-4.3
3	-8	3.6	4.2
3	-7	3.1	4.3
3	-6	2.8	1.6
3	-5	7.1	10.
3	-4	43.0	45.
3	-3	2.2	-4.5
3	-2	33.6	-28.8
3	-1	26.3	27.1
3	0	55.2	-50.7
3	1	39.4	41.5
3	2	37.1	33.7
3	3	47.5	-47.1
3	4	3.0	7.5
3	5	5.8	6.9
4	-8	25.2	-25.2
4	-7	15.6	-11.7
4	-6	19.1	20.5
4	-5	38.9	-42.7
4	-4	15.3	-15.1
4	-3	57.9	60.1
4	-2	27.8	-27.5
4	-1	34.6	-34.4
4	0	63.2	63.9
4	1	51.3	-49.5
4	2	25.4	23.5
4	3	27.9	34.
4	4	24.8	-23.1
5	-8	22.5	22.7
5	-7	18.4	-15.8
5	-6	21.2	-21.3
5	-5	25.0	21.8
5	-4	7.5	7.5
5	-3	8.0	-9.1
5	-2	9.5	11.1
5	-1	58.4	-52.7
5	0	14.6	-12.8
5	1	24.6	26.3
5	2	16.6	-18.6
5	3	12.9	11.8
5	4	4.2	5.
6	-7	14.3	13.4
6	-6	10.4	9.2
6	-5	20.0	-21.4
6	-4	27.3	25.7
6	-3	15.5	13.3
6	-2	24.4	-23.7
6	-1	62.7	64.5
6	0	10.9	-8.7
6	1	18.3	-18.1
6	2	22.7	23.2
6	3	16.2	-15.
6	4	3.5	4.5
7	-6	6.0	4.4
7	-5	3.1	5.4
7	-4	27.7	-31.1
7	-3	42.9	41.7
7	-2	5.3	-5.9
7	-1	27.3	-28.9

Table 2 (*cont.*)

K	L	|FOBS|	FCALC
7	0	35.9	38.4
7	1	15.3	-16.3
7	2	27.9	-27.4
8	-6	16.8	-18.4
8	-5	19.3	14.9
8	-4	21.3	22.8
8	-3	34.0	-34.5
8	-2	0.	4.6
8	-1	3.2	3.
8	0	36.2	-35.9
8	1	41.0	37.7
9	-3	16.0	17.
9	-2	22.6	-22.4
9	-1	3.4	4.4
9	0	3.4	-2.1
9	1	14.3	-18.8
9	2	22.0	19.6
H =	3		
-11	0	23.2	21.9
-11	1	22.5	-21.5
-11	2	25.2	25.
-10	-4	22.2	-22.9
-10	-3	3.6	1.6
-10	-2	25.9	26.4
-10	-1	30.3	-30.4
-10	0	12.9	-13.5
-10	1	18.8	19.9
-10	2	31.3	-31.2
-10	3	24.7	26.2
-10	4	16.8	17.7
-10	5	12.1	-11.9
-10	6	22.5	-18.[illegible]
-9	-4	27.7	28.9
-9	-3	3.4	0.2
-9	-2	14.1	-14.6
-9	-1	36.2	35.2
-9	0	34.9	-33.3
-9	1	14.3	-13.8
-9	2	30.4	27.8
-9	3	25.3	-23.
-9	4	10.6	-11.3
-8	-4	15.9	-14.3
-8	-3	26.0	24.4
-8	-2	19.4	-21.6
-8	-1	10.9	-14.6
-8	0	22.6	21.7
-8	1	3.0	2.1
-8	2	15.4	-16.7
-8	3	23.8	24.6
-8	4	33.1	-33.
-8	5	3.6	4.8
-7	-6	18.4	-17.8
-7	-5	17.0	15.8
-7	-4	15.2	-14.9
-7	-3	17.1	-15.5
-7	-2	48.3	46.
-7	-1	53.6	-48.5
-7	0	11.9	-9.2
-7	1	48.7	42.8
-7	2	15.7	11.3
-7	3	3.1	5.1
-7	4	24.9	22.4
-7	5	3.3	-2.3
-6	-5	25.6	-27.2
-6	-4	37.3	36.2
-6	-3	21.1	-18.
-6	-2	35.7	-33.7
-6	-1	20.4	17.7
-6	0	18.1	-14.8
-6	1	2.7	-1.9
-6	2	13.4	14.1
-6	3	19.5	-13.9
-6	4	3.0	-5.
-6	5	15.3	-13.1
-6	6	12.4	-12.7
-5	-6	17.9	20.6
-5	-5	11.6	12.7
-5	-4	28.6	-28.7
-5	-3	36.9	35.8
-5	-2	34.6	30.1
-5	-1	47.0	-45.5
-5	0	15.7	-14.4
-5	1	7.8	-9.9
-5	2	31.1	-30.8
-5	3	40.1	41.
-5	4	16.9	13.8
-5	5	9.3	-9.8
-5	6	20.1	19.1
-4	-7	18.2	17.7
-4	-6	14.5	-17.3
-4	-5	10.9	-14.5
-4	-4	20.5	18.6
-4	-3	43.7	-37.6
-4	-2	36.3	30.1
-4	-1	25.4	26.6
-4	0	18.9	16.1
-4	1	17.9	14.3
-4	2	19.0	17.8
-4	3	34.1	-33.5
-4	4	38.8	33.2
-4	5	5.4	5.6
-4	6	13.9	-14.7
-3	-7	3.3	2.1
-3	-6	13.9	13.
-3	-5	5.2	-9.8
-3	-4	25.4	24.6
-3	-3	11.7	19.9
-3	-2	2.2	-2.2
-3	-1	60.2	62.4
-3	0	42.2	41.9
-3	1	23.1	-24.4
-3	2	27.3	27.9
-3	3	22.0	20.2
-3	4	40.8	-41.7
-3	5	12.5	-9.9
-3	6	10.0	11.3
-2	-7	11.6	-14.4
-2	-6	7.6	-8.7
-2	-5	13.7	12.3
-2	-4	19.8	-17.2
-2	-3	18.0	22.2
-2	-2	8.5	5.2
-2	-1	322.5	-328.2
-2	0	17.2	18.5
-2	1	2.1	-8.4
-2	2	2.3	-0.1
-2	3	24.6	-25.5
-2	4	12.8	13.6
-2	5	5.4	-8.2
-2	6	3.3	-5.8
-1	-7	18.3	17.6
-1	-6	19.3	-16.3
-1	-5	25.4	-28.5
-1	-4	15.8	11.9
-1	-3	13.0	17.7
-1	-2	1.9	-0.2
-1	-1	66.5	69.3
-1	0	42.0	42.7
-1	1	17.1	-20.1
-1	2	20.7	20.
-1	3	24.5	22.6
-1	4	16.6	-14.6
-1	5	25.4	26.7
-1	6	5.9	-5.5
0	-8	3.4	3.6
0	-7	24.3	-23.5
0	-6	38.4	39.3
0	-5	25.0	-29.8
0	-4	21.2	-21.4
0	-3	23.2	24.1
0	-2	80.0	81.3
0	-1	26.2	-17.5
0	0	1.9	-2.7
0	1	2.1	-1.9
0	2	31.1	-28.9
0	3	20.4	-18.9
0	4	6.2	8.
0	5	15.7	-15.2
0	6	26.9	32.
1	-8	23.2	25.7
1	-7	8.2	7.2
1	-6	24.3	-25.5
1	-5	34.2	33.4
1	-4	2.3	1.8
1	-3	16.1	-15.1
1	-2	64.9	-64.
1	-1	14.9	15.3
1	0	21.9	23.3
1	1	22.1	19.3
1	2	21.3	19.6
1	3	13.8	-16.2
1	4	42.7	43.8
1	5	3.2	-3.8
2	-8	22.9	-23.
2	-7	5.3	-9.3
2	-6	8.3	7.
2	-5	50.0	-53.5
2	-4	18.5	19.6
2	-3	12.1	10.9
2	-2	25.5	-23.5
2	-1	6.8	12.2
2	0	32.3	32.3
2	1	37.8	-39.2
2	2	16.0	13.5
2	3	8.1	7.4
2	4	24.8	-24.3
2	5	9.3	7.6
3	-8	14.5	13.3
3	-7	3.1	2.8
3	-6	9.5	7.7
3	-5	19.7	16.
3	-4	27.2	28.5
3	-3	42.0	40.6
3	-2	2.3	-0.7
3	-1	42.9	-39.3
3	0	8.0	5.9
3	1	13.3	12.2
3	2	40.6	-37.1
3	3	7.4	-8.6
3	4	14.9	14.1
4	-7	11.0	11.3
4	-6	18.6	-22.7
4	-5	7.0	-8.2
4	-4	12.3	-9.4
4	-3	36.3	35.6
4	-2	27.8	-22.5
4	-1	41.2	42.
4	0	17.6	-16.4
4	1	21.0	-22.7
4	2	23.6	22.6
4	3	10.0	-9.
5	-7	3.[illegible]	-1.8
5	-6	3.0	2.
5	-5	13.0	-15.3
5	-4	28.1	-25.5
5	-3	2.7	3.7
5	-2	7.3	-5.5
5	-1	8.7	-9.2
5	0	22.8	21.4
5	1	6.0	5.1
5	2	17.0	-17.3
5	3	18.2	14.7
6	-7	6.8	8.8
6	-6	12.1	-13.4
6	-5	26.6	27.2
6	-4	5.2	-4.4
6	-3	25.4	-26.7
6	-2	5.1	4.5
6	-1	7.9	-7.2
6	0	3.0	-6.4
6	1	23.4	24.2
6	2	31.0	-29.7
7	-6	3.3	-2.3
7	-5	30.4	-30.7
7	-4	39.9	39.3
7	-3	8.2	9.4
7	-2	24.2	-22.1
7	-1	28.3	30.3
7	0	3.2	-3.1
7	1	24.0	-20.
8	-4	22.7	-17.4
8	-3	13.4	14.5
8	-2	11.7	10.9
8	-1	12.0	-12.3
8	0	18.9	16.3
9	-7	3.7	3.3
9	-6	11.9	-10.8
9	-5	20.5	18.9
9	-4	10.4	9.2
9	-3	14.6	-12.3
9	-2	6.3	-4.1
9	-1	18.8	20.3
9	0	3.6	-5.5
H =	4		
-11	0	19.6	-22.1
-11	1	13.9	12.2
-11	2	3.6	2.5
-11	3	21.1	-21.5
-11	4	18.7	20.4
-11	5	21.6	17.6
-11	6	23.9	-21.3
-10	-3	19.1	19.9
-10	-2	8.3	-11.6
-10	-1	3.5	1.1
-10	0	22.8	23.2
-10	1	23.0	-22.5
-10	2	9.8	7.
-10	3	23.0	22.7
-9	-4	3.6	7.
-9	-3	33.3	-30.9
-9	-2	28.7	29.1
-9	-1	22.7	-18.9
-9	0	28.5	-26.8
-9	1	37.6	36.2
-9	2	18.2	-20.9
-9	3	3.5	-1.3
-9	4	20.4	20.2
-9	5	25.3	-25.4
-9	6	13.0	12.7
-9	7	14.7	15.7
-8	-5	17.5	-15.6
-8	-4	17.7	17.5
-8	-3	3.3	-1.3
-8	-2	24.0	-23.3
-8	-1	36.3	36.9
-8	0	11.7	8.2
-8	1	33.5	-30.7
-8	2	27.1	27.9
-8	3	29.2	-29.6
-8	4	6.1	-4.9
-7	-5	6.1	5.2
-7	-4	22.5	-22.4
-7	-3	41.2	37.5
-7	-2	5.4	8.7
-7	-1	32.9	-30.3
-7	0	38.3	36.
-7	1	3.0	-1.2
-7	2	35.8	-38.6
-7	3	58.4	57.
-7	4	3.2	1.4
-7	5	16.8	-14.7
-6	-6	17.5	-19.8
-6	-5	3.3	5.6
-6	-4	18.7	17.8
-6	-3	41.3	-40.5
-6	-2	29.0	31.9
-6	-1	13.7	10.5
-6	0	33.9	-36.5
-6	1	25.1	26.8
-6	2	43.7	-45.2
-6	3	19.6	-18.2
-6	4	26.8	29.2
-6	5	3.3	1.8
-5	-6	30.5	27.1
-5	-5	13.3	-10.6
-5	-4	9.9	-8.4
-5	-3	20.6	20.
-5	-2	39.3	-35.1
-5	-1	5.5	2.5
-5	0	28.9	26.8
-5	1	41.0	-41.5
-5	2	29.8	27.
-5	3	19.1	-17.5
-5	4	16.4	-15.1
-5	5	24.6	24.8
-4	-7	27.6	-28.2
-4	-6	32.7	-36.1
-4	-5	28.2	26.2
-4	-4	36.8	-33.9
-4	-3	18.0	-15.
-4	-2	18.7	22.6
-4	-1	56.8	-57.3
-4	0	2.4	5.
-4	1	8.6	8.4
-4	2	44.2	-43.7
-4	3	41.6	41.4
-4	4	12.2	-12.
-4	5	17.5	-16.
-4	6	3.4	1.1
-4	7	3.7	4.1
-4	8	12.3	-13.
-3	-7	21.2	18.6
-3	-6	3.3	2.5
-3	-5	22.5	-20.
-3	-4	40.6	39.9
-3	-3	9.7	12.2
-3	-2	47.2	51.1
-3	-1	55.8	49.6
-3	0	15.2	-16.4
-3	1	4.8	3.8
-3	2	22.3	19.
-3	3	2.7	3.2
-3	4	17.9	19.2
-3	5	7.7	8.2
-2	-7	11.3	-14.
-2	-6	33.5	31.9
-2	-5	19.4	-17.2
-2	-4	34.3	-34.5
-2	-3	41.4	42.7
-2	-2	122.0	-123.5
-2	-1	72.0	67.4
-2	0	7.3	7.8
-2	1	18.9	-19.1
-2	2	2.5	-0.7
-2	3	12.7	13.1
-2	4	16.1	-17.2
-2	5	10.1	14.
-1	-7	8.5	-13.8
-1	-6	12.3	-9.9
-1	-5	45.3	48.9
-1	-4	25.4	-28.2
-1	-3	22.3	-17.6
-1	-2	100.4	106.1
-1	-1	28.9	-30.3
-1	0	9.2	-6.2
-1	1	16.1	12.8
-1	2	45.2	-46.5
-1	3	9.2	-6.6
-1	4	21.7	22.
-1	5	16.5	-14.5
0	-8	19.1	-21.
0	-7	30.2	28.1
0	-6	15.6	-17.9
0	-5	35.1	-33.7
0	-4	33.1	32.2
0	-3	5.8	6.3
0	-2	23.1	-21.9
0	-1	34.3	31.1
0	0	9.6	-6.2
0	1	16.7	-22.
0	2	23.3	-21.
0	3	8.1	8.
0	4	5.5	-7.8
0	5	17.0	19.5
0	6	24.7	-27.2
1	-8	16.1	18.3
1	-7	20.8	-23.7
1	-6	19.0	20.1
1	-5	11.2	-10.
1	-4	14.3	-13.3
1	-3	32.0	31.6
1	-2	15.7	-16.5
1	-1	35.6	-37.3
1	0	42.5	38.2
1	1	4.7	4.1
1	2	12.9	-14.4
1	3	8.1	8.6
1	4	5.7	-6.3
2	-8	3.3	-2.3
2	-7	17.1	17.7
2	-6	41.3	-38.9
2	-5	18.0	22.4
2	-4	4.5	7.8
2	-3	30.6	-26.1
2	-2	7.2	7.2
2	-1	12.5	-14.
2	0	33.2	-31.3
2	1	37.2	29.9
2	2	2.9	-0.
2	3	3.0	-4.3
2	4	11.2	12.7
3	-7	3.1	-1.3
3	-6	21.5	23.9
3	-5	22.4	-22.3
3	-4	13.4	-12.1
3	-3	7.1	9.5
3	-2	2.6	-3.5
3	-1	42.3	39.1
3	0	21.5	20.
3	1	36.8	-36.3
3	2	7.6	10.2
3	3	9.8	12.1
4	-7	20.1	-25.1
4	-6	3.0	6.
4	-5	10.0	14.4
4	-4	2.8	5.2
4	-3	10.3	-9.6
4	-2	25.4	26.
4	-1	33.1	-32.
4	0	3.6	3.8
4	1	3.0	0.5
4	2	30.4	-29.3
5	-7	12.5	10.5
5	-6	3.1	-1.5
5	-5	3.0	-1.7
5	-4	5.2	4.5
5	-3	12.8	-12.5
5	-2	2.9	-0.
5	-1	18.9	18.4
5	0	25.6	26.9
5	1	9.3	-9.6
5	2	17.2	18.8
5	3	19.1	19.7
6	-6	10.5	11.2
6	-5	27.7	-26.
6	-4	3.1	0.6
6	-3	18.1	18.2
6	-2	3.1	-5.5
6	-1	13.7	-13.6
6	0	22.7	21.7
6	1	16.2	-13.6
7	-5	26.2	27.6
7	-4	3.3	1.
7	-3	3.2	-0.9
7	-2	3.3	-2.6
7	-1	11.0	-11.3
7	0	17.8	-16.1
8	-5	28.5	-28.7
8	-4	3.4	-2.9
8	-3	3.4	1.5
8	-2	3.4	-6.1
8	-1	3.5	-3.
8	0	13.0	10.2
H =	5		
-10	-1	25.8	23.6
-10	0	3.5	-5.3
-10	1	37.4	-36.7
-10	2	22.2	23.6
-9	-3	17.2	17.3
-9	-2	19.2	-16.
-9	-1	34.8	-35.2
-9	0	27.0	25.
-9	1	3.4	-0.2
-9	2	20.3	-17.8
-9	3	29.3	30.5
-9	4	18.4	-17.7
-8	-4	3.5	-1.
-8	-3	21.6	-18.5
-8	-2	21.4	21.9
-8	-1	24.7	21.9
-8	0	14.6	-15.5
-8	1	17.2	16.6
-8	2	25.2	-22.7
-8	3	11.9	-13.4
-8	4	27.5	29.3
-7	-5	14.1	-13.6
-7	-4	3.4	0.9
-7	-3	14.4	13.1
-7	-2	22.8	-21.3
-7	-1	16.8	15.6
-7	0	5.4	4.2
-7	1	30.1	-32.2
-7	2	36.2	40.6
-7	3	5.7	-5.9
-7	4	24.8	-23.7
-7	5	29.1	30.7
-6	-5	34.0	31.5
-6	-4	36.9	-35.3
-6	-3	9.0	-6.6
-6	-2	30.4	29.6
-6	-1	43.6	-43.
-6	0	12.1	11.
-6	1	19.8	21.9
-6	2	45.8	-44.6
-6	3	24.5	26.7
-6	4	5.8	11.1
-6	5	19.7	-20.5
-5	-6	3.5	3.8
-5	-5	13.5	-13.9
-5	-4	39.7	40.3
-5	-3	18.7	-16.2
-5	-2	2.7	0.4
-5	-1	90.9	90.8
-5	0	50.3	-54.7
-5	1	4.8	6.7
-5	2	5.1	8.3
-5	3	25.7	-28.3
-5	4	29.6	32.6
-5	5	3.4	-0.8
-4	-6	21.7	22.9
-4	-5	6.9	-8.8
-4	-4	23.4	-21.
-4	-3	52.9	53.
-4	-2	64.0	-64.1
-4	-1	31.8	30.8
-4	0	33.2	29.5
-4	1	42.9	-42.4
-4	2	15.4	15.7
-4	3	20.7	19.6
-4	4	27.9	-28.1
-3	-7	3.5	4.8
-3	-6	36.3	-35.9
-3	-5	32.9	33.3
-3	-4	5.7	-3.6
-3	-3	27.5	-27.1
-3	-2	27.5	28.8
-3	-1	68.8	-69.
-3	0	28.9	-29.1
-3	1	31.6	32.7
-3	2	31.0	-34.
-3	3	3.0	-0.2
-3	4	7.4	12.
-2	-7	14.3	17.2
-2	-6	10.3	9.5
-2	-5	29.3	-28.
-2	-4	2.7	1.8
-2	-3	17.1	-23.3
-2	-2	12.7	14.1
-2	-1	26.7	27.7
-2	0	9.9	-13.8
-2	1	4.6	-3.4
-2	2	16.5	17.3
-2	3	3.0	-1.4
-2	4	11.6	9.8
-1	-7	17.3	-12.5
-1	-6	28.8	29.7
-1	-5	16.4	19.9
-1	-4	46.8	-49.9
-1	-3	23.8	19.6
-1	-2	23.2	24.8
-1	-1	19.3	-21.4
-1	0	42.2	39.4
-1	1	10.4	-6.
-1	2	21.6	-23.1
-1	3	17.1	18.8
-1	4	34.5	-32.1
0	-7	18.3	21.4
0	-6	32.8	-35.8
0	-5	18.1	18.8
0	-4	14.8	11.2
0	-3	21.3	-23.4
0	-2	31.1	33.2
0	-1	7.2	-3.3
0	0	24.3	-20.9
0	1	31.2	34.3
0	2	5.2	-7.3
0	3	5.8	-3.
0	4	24.1	25.9
1	-7	3.2	-1.
1	-6	13.1	12.
1	-5	40.7	-40.6
1	-4	15.4	16.5
1	-3	21.9	18.8
1	-2	28.3	-28.1
1	-1	23.5	22.6
1	0	23.5	-24.7
1	1	6.1	-6.4
1	2	31.2	31.5
1	3	3.2	-3.9
2	-7	21.0	-24.1
2	-6	19.4	21.6
2	-5	29.8	34.1
2	-4	27.2	-30.3
2	-3	10.0	9.9
2	-2	2.7	6.5
2	-1	45.1	-44.8
2	0	37.7	36.8
2	1	14.7	-14.8
2	2	14.7	-17.5
2	3	5.9	7.9
3	-7	25.8	28.1
3	-6	22.0	-17.7
3	-5	12.9	-13.5
3	-4	29.5	26.1
3	-3	2.8	-2.4
3	-2	16.3	17.5
3	-1	15.9	13.1
3	0	10.8	-10.1
3	1	5.5	6.1
3	2	3.2	-0.
3	3	3.4	-0.1
4	-7	21.2	-19.
4	-6	27.2	28.6
4	-5	6.2	-6.1

Table 2 (*cont.*)

K	L	|FOBS|	FCALC	K	L	|FOBS|	FCALC	K	L	|FOBS|	FCALC	K	L	|FOBS|	FCALC	K	L	|FOBS|	FCALC	K	L	|FOBS|	FCALC
4	-4	25.3	-27.2	-5	-2	14.5	12.1	0	-5	16.9	15.8	H =	7			-1	-6	3.2	-5.6	7	-6	13.2	-12.6
4	-3	16.8	14.6	-5	-1	44.3	-45.4	0	-4	25.7	-26.	-8	-2	6.2	-6.5	-1	-5	6.5	-9.9	7	-5	10.5	-8.3
4	-2	46.8	-45.1	-5	0	12.9	-8.5	0	-3	19.5	17.2	-8	-1	3.4	-1.1	-1	-4	20.2	22.5	7	-4	17.4	11.5
4	-1	3.0	-3.7	-5	1	26.5	27.3	0	-2	19.5	17.7	-8	0	12.4	13.6	-1	-3	16.3	-15.1	7	-3	15.3	-12.5
4	0	16.9	17.5	-5	2	27.2	-27.2	0	-1	61.2	-56.8	-8	1	3.4	-1.4	-1	-2	18.6	19.	7	-2	3.9	-9.3
4	1	12.8	-14.	-5	3	18.3	17.6	0	0	30.3	28.8	-7	-4	8.7	-9.7	-1	-1	6.3	6.	7	-1	4.0	-2.7
5	-6	13.5	-10.4	-4	-6	3.3	-0.3	0	1	8.0	8.5	-7	-3	3.4	4.9	-1	0	34.7	-33.5	7	0	11.9	-7.2
5	-5	21.3	23.8	-4	-5	19.0	-23.9	0	2	18.6	-19.9	-7	-2	17.6	21.5	-1	1	17.7	17.4	H =	8		
5	-4	25.2	-26.8	-4	-4	34.5	31.8	0	3	25.7	22.1	-7	-1	21.8	-19.5	0	-7	3.4	3.2	-6	-3	13.9	16.5
5	-3	3.1	-5.1	-4	-3	5.7	-3.6	1	-7	16.8	18.9	-7	0	3.2	3.	0	-6	8.2	7.1	-6	-2	2.8	-5.1
5	-2	18.2	18.7	-4	-2	66.5	71.	1	-6	28.7	-32.2	-7	1	8.8	8.8	0	-5	8.9	-7.7	-6	-1	2.8	-6.7
5	-1	17.3	-17.2	-4	-1	34.3	34.8	1	-5	19.4	-24.2	-6	-5	3.5	4.3	0	-4	0.	-4.1	-6	0	3.0	-1.4
5	0	3.3	3.3	-4	0	5.0	7.1	1	-4	16.6	12.6	-6	-4	13.6	14.2	0	-3	22.3	23.5	-5	-4	10.0	11.
6	-5	26.2	-28.	-4	1	9.5	-13.1	1	-3	26.8	-25.2	-6	-3	3.2	-0.8	0	-2	15.9	-14.2	-5	-3	2.6	2.3
6	-4	25.0	23.5	-4	2	42.7	44.8	1	-2	19.0	18.6	-6	-2	9.3	8.3	0	-1	16.2	18.	-5	-2	6.6	10.3
6	-3	11.8	11.1	-4	3	22.7	-26.4	1	-1	9.4	13.3	-6	-1	23.1	23.2	0	0	3.2	-1.7	-5	-1	9.6	9.4
6	-2	7.4	-6.8	-4	4	3.4	1.5	1	0	28.3	-27.1	-6	0	13.2	-12.4	0	1	20.8	-20.6	-5	0	2.8	-3.7
6	-1	13.5	12.2	-3	-7	15.3	-13.4	1	1	35.4	33.8	-6	1	3.2	4.7	1	-6	10.2	-10.8	-4	-5	3.0	10.4
6	0	24.3	-20.	-3	-6	28.9	30.4	1	2	14.0	14.9	-6	2	4.4	7.5	1	-5	23.8	24.	-4	-4	2.7	4.
H =	6			-3	-5	10.3	8.7	2	-7	3.3	-0.2	-5	-5	6.0	-5.3	1	-4	3.1	-1.7	-4	-3	7.8	-12.
-9	-2	8.1	-8.4	-3	-4	39.4	-40.9	2	-6	23.9	21.8	-5	-4	13.9	-17.2	1	-3	5.5	-6.9	-4	-2	6.5	9.
-9	-1	3.5	5.	-3	-3	34.8	36.7	2	-5	12.7	-12.3	-5	-3	8.7	-7.4	1	-2	5.5	6.9	-4	-1	9.1	-12.5
-9	0	12.4	13.	-3	-2	50.8	-48.9	2	-4	11.3	-13.7	-5	-2	26.2	-22.9	1	-1	29.1	-27.8	-4	0	5.4	8.1
-9	1	31.4	-31.2	-3	-1	53.3	-50.5	2	-3	37.5	35.9	-5	-1	16.6	-16.9	1	0	13.9	15.7	-3	-5	9.4	13.7
-8	-4	3.5	-2.	-3	0	53.5	54.8	2	-2	60.4	-57.3	-5	0	21.5	24.4	2	-5	28.1	-27.5	-3	-4	5.3	-3.4
-8	-3	6.2	10.4	-3	1	16.0	-14.3	2	-1	13.4	15.5	-5	1	19.0	-18.6	2	-4	32.2	33.1	-3	-3	10.3	-15.7
-8	-2	17.9	16.7	-3	2	28.6	-27.7	2	0	22.3	22.1	-5	2	10.5	-14.1	2	-3	19.9	-21.	-3	-2	2.4	1.4
-8	-1	16.1	-16.3	-3	3	24.5	20.9	2	1	28.3	-25.1	-4	-6	3.4	-2.7	2	-2	3.2	3.2	-3	-1	5.7	7.3
-8	0	3.3	0.5	-3	4	25.6	-24.2	3	-6	3.2	-6.2	-4	-5	5.8	7.5	2	-1	23.4	23.6	-3	0	5.4	-8.2
-8	1	13.9	14.7	-3	5	3.6	4.2	3	-5	39.7	39.	-4	-4	9.5	8.6	2	0	16.2	-15.8	-2	-5	5.0	-4.8
-8	2	16.0	-16.2	-2	-7	3.3	-2.1	3	-4	9.5	-11.6	-4	-3	43.7	46.7	3	-4	16.8	-14.	-2	-4	4.3	3.2
-8	3	15.0	17.7	-2	-6	8.5	-7.6	3	-3	7.3	-6.4	-4	-2	28.0	-24.1	3	-3	20.3	16.7	-2	-3	2.4	3.5
-7	-4	5.5	7.1	-2	-5	22.9	19.8	3	-2	24.6	26.2	-4	-1	7.2	5.6	3	-2	16.3	-17.5	-2	-2	4.9	-10.5
-7	-3	22.7	-20.5	-2	-4	6.3	4.7	3	-1	23.9	-20.6	-4	0	14.2	-16.4	3	-1	24.5	-24.7	-2	-1	6.4	4.1
-7	-2	3.2	5.6	-2	-3	77.0	-81.5	3	0	3.2	-6.8	-4	1	29.8	27.5	3	0	27.3	25.3	-2	0	4.5	5.4
-7	-1	32.4	33.7	-2	-2	43.0	45.7	4	-8	17.9	-17.6	-4	2	11.7	-12.6	3	1	24.4	-26.	-1	-5	2.9	6.7
-7	0	14.5	-16.4	-2	-1	18.2	22.8	4	-7	12.4	18.8	-3	-6	3.3	-4.2	3	2	19.5	-18.	-1	-4	5.7	-8.4
-7	1	19.1	16.7	-2	0	31.6	-31.	4	-6	13.5	-20.5	-3	-5	3.1	-2.1	5	-8	11.2	-12.	-1	-3	2.5	-0.8
-7	2	3.2	1.6	-2	1	32.4	30.5	4	-5	13.3	-12.8	-3	-4	11.0	9.1	5	-7	3.7	3.7	-1	-2	10.8	12.2
-7	3	28.9	-27.5	-2	2	8.9	12.4	4	-4	33.2	32.5	-3	-3	32.4	-34.6	5	-6	3.6	-7.7	-1	-1	2.8	-6.1
-7	4	15.5	14.4	-2	3	8.1	-9.1	4	-3	15.1	-12.7	-3	-2	15.7	-16.9	5	-5	17.5	-16.1	-1	0	3.0	-6.7
-6	-6	21.5	21.3	-2	4	18.2	18.8	4	-2	3.2	1.4	-3	-1	23.9	22.	5	-4	3.5	5.6	0	-4	8.5	10.4
-6	-5	13.4	-14.9	-1	-7	8.1	10.	4	-1	17.9	20.5	-3	0	3.0	1.5	5	-3	3.5	5.4	0	-3	2.7	-4.
-6	-4	3.3	-5.8	-1	-6	3.1	3.	4	0	17.3	-15.	-3	1	17.7	-19.1	5	-2	3.6	3.	0	-2	4.9	6.6
-6	-3	19.2	20.8	-1	-5	31.8	-35.7	5	-6	28.3	28.2	-3	2	23.4	25.7	5	-1	17.6	18.	0	-1	3.0	1.2
-6	-2	29.4	-31.1	-1	-4	18.3	18.5	5	-5	19.0	-23.7	-2	-6	3.3	4.2	5	0	3.7	-6.7	0	0	3.2	-1.
-6	-1	28.8	-28.7	-1	-3	57.1	59.	5	-4	16.9	-16.	-2	-5	7.2	8.5	6	-8	20.7	19.1	5	0	9.9	-11.9
-6	0	22.5	25.1	-1	-2	45.9	-44.7	5	-3	28.3	27.2	-2	-4	31.2	-32.	6	-7	13.8	-11.2	6	-7	4.6	11.8
-6	1	24.0	-25.9	-1	-1	12.4	15.7	5	-2	17.2	-17.3	-2	-3	20.0	18.9	6	-6	19.1	20.3	7	-4	8.6	-8.2
-6	2	16.4	18.5	-1	0	2.8	-0.9	5	-1	5.5	-2.4	-2	-2	12.3	11.7	6	-5	8.3	11.6	7	-3	3.4	-0.8
-6	3	3.3	-3.	-1	1	38.1	-38.	5	0	21.4	19.3	-2	-1	20.7	-21.6	6	-4	8.7	-10.9	7	-2	11.7	12.3
-5	-6	22.0	-21.	-1	2	17.7	17.1	6	-4	8.4	-7.4	-2	0	29.5	32.5	6	-3	8.3	8.5	7	-1	9.8	-9.7
-5	-5	16.1	12.1	-1	3	21.9	-24.5	6	-3	12.5	-14.3	-2	1	11.3	9.7	6	-2	8.4	8.5				
-5	-4	3.1	-1.2	0	-7	15.5	-14.9	6	-2	13.6	17.4	-2	2	32.9	-32.7	6	-1	12.9	-11.8				
-5	-3	34.1	-33.	0	-6	18.4	19.6	6	-1	14.5	-16.6	-2	3	28.7	29.4	6	0	9.2	11.8				

In view of the chemical evidence (above and Fischer & Orth, 1937) for the presence of two vinyl groups per molecule, the following possibilities for the arrangement of the vinyl groups in the unit cell exist:

(i) Centrosymmetric pairs of vinyl groups at any two positions among *A*2, *A*3, *D*2, and *D*3. (This arrangement would give rise to only two peaks per molecule).

(ii) Non-centrosymmetric arrangement in pairs, with one pair of positions occupied by vinyl groups on one molecule, and the remaining pair of positions occupied on the other molecule of the unit cell.

(iii) Disordered vinyl groups, distributed among the four positions in pairs or singly, at random.

Case (i) was rapidly rejected both by least-squares refinement and by F_o–F_c syntheses. It was then found that the locations of peaks corresponding to atoms *A*2*β* and *A*3*β* of the same molecule were only 2·6 Å apart, so that both these atoms could not reasonably be placed on the same molecule. Thus the only permissible combinations of vinyl groups are at *A*2 and *D*2 of one molecule and at *A*3 and *D*3 of the other molecule, or alternatively at *A*2, *D*3 and *A*3, *D*2. The former arrangement corresponds to the chemical structure deduced by Fischer; the latter arrangement embodies two isomers of porphyrin not found in nature and is not considered further.

There are then (at least approximately) equal numbers of molecules with vinyl groups at *A*2 and *D*2, and molecules with vinyl groups at *A*3 and *D*3, in the crystal. The two possible arrangements of these molecules, disordered and non-centrosymmetric, gave nearly identical values of *R*, individual temperature factors, and equally satisfactory F_o–F_c syntheses through several cycles of refinement. Optical and physical tests for distinguishing between $P1$ and $P\bar{1}$ were impractical because of the strong light absorption and poor quality of the crystals. No decision could be made on the basis of packing. Attempts to define the vinyl positions further were not felt worthwhile. The space group was chosen as $P\bar{1}$ since the behavior of the rest of the structure gave no justification for doubling the number of independent parameters.

Four 'half-carbon' atoms were placed at the four low peaks of the current F_o–F_c synthesis, with temperature factors of 9·0 Å^2 in accord with the diffuseness of the peaks. Only half-atom *A*2*β* seemed to refine satisfactorily by least squares; positions of the other three were adjusted as indicated by F_o–F_c syntheses.

During final stages of refinement, several atoms of the propionate groups were allowed anisotropic tem-

Table 3. *Final structure parameters*

(*a*) Fractional coordinates *x*, *y*, *z* along *a*, *b*, *c* for one molecule, with standard deviations in units of 0·001 Å. Temperature factors and standard deviations in Å².

Atom	x	σ_x	y	σ_y	z	σ_z	B	σ_B
Fe^{3+}	0·3137	2	0·6209	2	0·3448	2		
Cl$^-$	0·1501	5	0·6586	5	0·3779	5		
*A*1	0·3815	15	0·7472	15	0·1480	15	4·49	0·34
*A*2	0·3347	19	0·7409	18	0·0040	18	5·47	0·41
*A*3	0·2375	18	0·6489	17	−0·0652	17	4·68	0·38
*A*4	0·2271	15	0·5945	15	0·0367	15	4·20	0·33
AB	0·1457	16	0·4904	15	0·0073	15	4·27	0·34
*B*1	0·1457	15	0·4318	15	0·0978	15	4·11	0·33
*B*2	0·0751	17	0·3222	16	0·0624	17	4·96	0·37
*B*3	0·1123	17	0·2931	16	0·1768	17	4·73	0·37
*B*4	0·2034	16	0·3819	15	0·2873	16	4·42	0·35
BC	0·2589	15	0·3840	14	0·4182	14	4·26	0·33
*C*1	0·3427	16	0·4710	15	0·5220	16	4·37	0·35
*C*2	0·3987	16	0·4744	15	0·6630	16	4·09	0·34
*C*3	0·4753	16	0·5709	15	0·7355	15	4·06	0·34
*C*4	0·4664	16	0·6321	15	0·6380	16	4·68	0·35
CD	0·5384	15	0·7386	14	0·6721	14	4·71	0·33
*D*1	0·5401	16	0·7979	15	0·5793	15	4·54	0·35
*D*2	0·6287	17	0·9066	16	0·6148	17	4·77	0·37
*D*3	0·6124	17	0·9268	17	0·4953	18	5·18	0·39
*D*4	0·5174	16	0·8390	15	0·3851	15	4·49	0·35
DA	0·4744	16	0·8313	15	0·2511	16	5·02	0·36
*A*2α	0·3989	21	0·8348	20	−0·0431	20	7·41	0·48
*A*2β	0·3622	46	0·8254	44	−0·1761	44	8·61	1·12
*A*3α	0·1494	18	0·6008	17	−0·2148	18	6·15	0·42
*A*3β	0·1920		0·6359		−0·3045		9·00	
*B*2α	−0·0218	18	0·2540	17	−0·0765	18	5·96	0·41
*B*3α	0·0750	21	0·1797	18	0·1925	18	6·53	0·44
*B*3β	−0·0443	22	0·1539	21	0·2329	25		
*B*3γ	−0·0884	27	0·0455	21	0·2375	28		
O*B*1	−0·1928	27	−0·0199	21	0·1609	23		
O*B*2	−0·0165	23	0·0169	21	0·3239	28		
*C*2α	0·3705	17	0·3744	16	0·7112	16	5·28	0·37
*C*2β	0·2343	19	0·3439	18	0·7236	18	6·03	0·41
*C*2γ	0·1906	27	0·2332	25	0·7348	28	7·04	0·55
O*C*1	0·0875	19	0·1722	16	0·6425	18		
O*C*2	0·2526	17	0·2097	12	0·8280	16		
*C*3α	0·5519	18	0·6117	17	0·8850	17	5·59	0·40
*D*2α	0·7113	20	0·9770	19	0·7631	19	7·02	0·46
*D*2β	0·6655		0·9717		0·8622		9·00	
*D*3α	0·6876	20	1·0358	19	0·4780	20	7·51	0·47
*D*3β	0·7400		1·0440		0·3870		9·00	
N*A*	0·3111	12	0·6537	11	0·1635	12	4·20	0·26
N*B*	0·2218	12	0·4684	12	0·2343	12	4·45	0·27
N*C*	0·3856	12	0·5715	11	0·5106	12	4·35	0·26
N*D*	0·4759	12	0·7575	11	0·4423	12	4·52	0·26

(*b*) Assigned fractional coordinates of hydrogen atoms included in final structure factor calculations

Bonded to atom	x	y	z
*B*3α	0·0455	0·1242	0·0989
*B*3α	0·1565	0·1737	0·2711
*B*3β	−0·0131	0·2065	0·3384
*B*3β	−0·1237	0·1707	0·1668
*C*2α	0·3651	0·3109	0·6346
*C*2α	0·4458	0·3857	0·8062
*C*2β	0·2453	0·3985	0·8142
*C*2β	0·1625	0·3523	0·6354
AB	0·0748	0·4527	−0·0974
BC	0·2337	0·3096	0·4433
CD	0·5972	0·7773	0·7784
DA	0·5188	0·9008	0·2234
*B*2α	−0·1211	0·2266	−0·0859
*B*2α	0·0031	0·1875	−0·1047
*B*2α	−0·0175	0·3019	−0·1490
*C*3α	0·4937	0·6281	0·9344
*C*3α	0·5797	0·5500	0·9172
*C*3α	0·6415	0·6822	0·9132
O*B*1–O*C*2	−0·2237	−0·1156	0·1668
O*B*2–O*C*1	−0·0521	−0·0783	0·3409

Table 3 (*cont.*)

(*c*) Components of anisotropic temperature factors and their standard deviations, multiplied by 10^4, defined by: $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$

Atom	B_{11}	σ	B_{22}	σ	B_{33}	σ	B_{12}	σ	B_{13}	σ	B_{23}	σ
B3β	188	31	107	20	379	46	126	38	246	63	214	47
B3γ	376	47	50	17	486	57	121	43	401	84	247	49
O*B*1	502	46	69	17	383	41	45	41	15	66	230	41
O*B*2	292	35	85	17	656	60	13	35	122	70	331	52
O*C*1	313	28	94	13	323	29	68	32	−26	50	176	32
O*C*2	305	27	62	10	221	24	−11	25	−67	42	105	26
Fe^{3+}	105	3	49	2	117	3	61	4	72	5	61	4
Cl$^-$	132	6	97	4	184	7	124	8	128	11	88	8

perature factors, as were the iron and chlorine atoms. Twenty hydrogen atoms (all except those on the *A* and *D* side groups) were included but not refined, with temperature factors of 9·0 Å^2.

Table 4. *Cartesian coordinates* (Å) *for one molecule*

Origin is at center of nitrogen square,
x' normal to plane of Fig. 3, directed upward.

Atom	x'	y'	z'
Fe^{3+}	−0·475	−0·006	0·010
Cl$^-$	−2·693	−0·047	0·056
*A*1	0·202	2·379	−1·867
*A*2	0·305	2·686	−3·293
*A*3	0·134	1·566	−4·006
*A*4	−0·016	0·524	−3·008
AB	−0·088	−0·844	−3·310
*B*1	−0·048	−1·874	−2·401
*B*2	0·063	−3·263	−2·740
*B*3	0·219	−3·925	−1·578
*B*4	0·176	−3·001	−0·479
BC	0·253	−3·293	0·837
*C*1	0·169	−2·386	1·863
*C*2	0·201	−2·696	3·276
*C*3	0·098	−1·581	3·987
*C*4	−0·030	−0·516	2·996
CD	−0·099	0·842	3·328
*D*1	−0·116	1·893	2·399
*D*2	−0·021	3·314	2·766
*D*3	0·138	3·935	1·592
*D*4	0·129	3·012	0·491
DA	0·243	3·276	−0·832
A2α	0·563	4·152	−3·730
A2β	0·754	4·407	−5·034
A3α	0·087	1·282	−5·506
A3β	0·681	2·123	−6·327
B2α	0·013	−3·851	−4·134
B3α	0·521	−5·458	−1·382
B3β	−0·792	−6·197	−1·147
B3γ	−0·554	−7·647	−1·071
O*B*1	−0·959	−8·433	−1·888
O*B*2	0·095	−8·124	−0·124
C2α	0·381	−4·155	3·780
C2β	−0·975	−4·894	3·730
C2γ	−0·743	−6·395	3·872
O*C*1	−1·100	−7·070	2·905
O*C*2	−0·265	−6·856	4·864
C3α	0·068	−1·413	5·476
D2α	−0·183	3·863	4·226
D2β	−1·057	3·346	5·106
D3α	0·295	5·509	1·440
D3β	1·189	6·045	0·648
N*A*	0·000	1·013	−1·739
N*B*	−0·001	−1·714	−1·032
N*C*	0·000	−1·012	1·728
N*D*	−0·001	1·717	1·045

Results and discussion

Observed and calculated structure factors are listed in Table 2. The final value of *R* for all 1566 reflections equally weighted is 0·095. The 230 observed reflections below the limit of reliable measurement are given values corresponding to one third the minimum measurable intensity (Hamilton, 1955).

Atomic parameters and calculated standard deviations are given in Table 3. Positions of all atoms of one molecule except hydrogen are given in Cartesian coordinates in Table 4. Distances and angles within a molecule are given in Figs. 3 and 4; values are given to four digits for purposes of record only.

The four nitrogen atoms very nearly form a square, planar within 0·01 Å. The iron atom lies 0·475 ± 0·01 Å along the normal through the center of the square (*below* the plane of Fig. 3), and the chlorine atom lies 2·218 ± 0·006 Å beyond the iron atom. The angle subtended at any nitrogen atom by the iron atom and the center of the square is 13·3 ± 0·3°. The iron–nitrogen distances are 2·062 ± 0·01 Å. All uncertainties are expressed as calculated standard deviations.

The iron atom is linked to five atoms. Opposite the chlorine atom is *C2α* of another molecule, at 3·85 Å from the iron atom and 3·51 Å from atom N*D*. The iron atom in sperm whale met-myoglobin has also

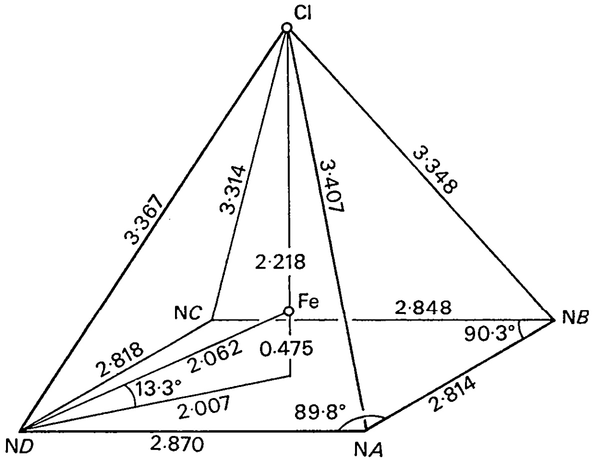

Fig. 4. Central region of the molecule. Nomenclature as in Fig. 3.

been observed to lie outside the mean plane of the porphyrin ring, although it is linked to six atoms (Kendrew, 1963). The nearest neighbors of the chlorine atom are *A3β* at 3·40 Å, *B2α* at 3·69 Å, and *A3α* at 3·86 Å. The chlorine atom is displaced from the normal to the nitrogen square by 0·08 Å, toward *A3β*.

Each pyrrole residue is planar within the accuracy of the atomic positions, about 0·02 Å. The porphyrin ring is puckered; each of the pyrrole residues is tilted 6 or 7° relative to the nitrogen plane, to form a largely convex surface as viewed from the iron atom. The pyrrole residues *A* and *D* are coplanar within 5°, and residues *B* and *C* within 4°; the two pairs of residues are inclined to each other by about 13°. Bridge atoms *AB* and *CD* lie 0·1 Å below the plane of Fig. 3, while atoms *AD* and *BC* lie 0·2 Å above the plane.

It will be noted from Fig. 3 that the internal angles of each pyrrole residues are asymmetrical; the pattern of angles in any one residues is mirrored in the others through lines joining opposite methene bridge atoms, consistent with the puckering of the porphyrin ring. Average bond lengths and angles of the pyrrole residues, reckoned on the basis of this approximate symmetry, are given in Fig. 5, with the 'hand' corresponding to that of residues *A* and *C*.

It was concluded (see *Structure determination*) that vinyl groups occur at *A*2 and *D*2 on some molecules, and at *A*3 and *D*3 on others. Efforts to distinguish between the two possibilities, a disordered structure and a non-centrosymmetric structure, were unsuccessful. If the structure is disordered, there must be two isomers of chlorohemin distinguished by the relative positions of the iron atom and vinyl groups. If the structure is non-centrosymmetric, there *might* be only one isomer.

The carboxyl groups of propionate groups attached to pyrrole residues *B* and *C* of one molecule are hydrogen-bonded to carboxyl groups *C* and *B*, respectively, of one other molecule. The distances from atom O*B*1 to O*C*2, and from O*B*2 to O*C*1, are respectively 2·58 Å and 2·66 Å; it will be clear from the following that these values are approximate. Atom *D3β* lies only 2·9 Å from *B3γ* and O*B*1, and 3·2 Å from O*B*2, of an adjacent molecule. The close approaches may account for the 8° inclination between planes of hydrogen-bonded carboxyl groups. Since *D3β* is present in only half the molecules, the pronounced 'thermal' anisotropies and high standard deviations associated with the carboxyl groups may be consequences of the two slightly different positions of these groups.

All other intermolecular distances are normal; the next closest aproaches are 3·40 Å between chlorine and *A*3 atoms, and 3·40 Å between two *AB* methene bridge atoms.

Several points of interest arise from comparisons among related structures (Table 5). In all, the four nitrogen atoms are coplanar, but only in the case of chlorohemin does the metal atom lie outside this plane. The metal–nitrogen distance is greater in chlorohemin than in the other structures, and would remain so (2·01 Å) if the iron atom were in the plane. Another feature of chlorohemin is the short bond between atoms 2 and 3 of the pyrrole residues, corresponding to a bond order of about two (Coulson, 1961).

The following internal evidence supports the conclusion that the structure found is the correct one: the coplanarity of the four nitrogen atoms, the planarity of each pyrrole residue, agreement among chemically equivalent parameters, and the reasonable packing arrangement.

Thanks are due especially to Prof. W. E. Love for suggesting this investigation and for constant encouragement and advice, to Prof. J. D. H. Donnay and

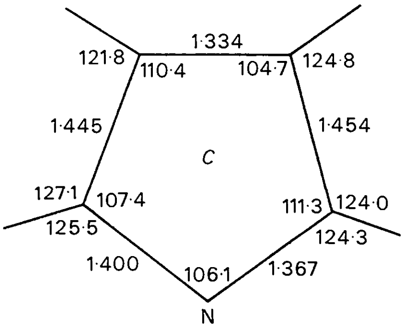

Fig. 5. Average bond lengths and angles of the pyrrole residues. See text for details.

Table 5. *Comparison of bond lengths* (Å) *among related structures*

Entries for structure (7) are mobile bond orders. (1) α-Chlorohemin; (2) nickel etioporphyrin (Crute, 1959); (3) nickel phthalocyanine (Robertson & Woodward, 1937); (4) analogue of nickel phthalocyanine (Speakman, 1953); (5) hexacarboxylic acid derivative of vitamin B_{12} (Hodgkin, Pickworth, Robertson, Prosen, Sparks & Trueblood, 1959); (6) pyrrole (Bak, Christensen, Hansen & Rastrup-Andersen, 1956); (7) porphyrin (Pullman & Perault, 1959).

	Structure						
Bond	(1)	(2)	(3)	(4)	(5)	(6)	(7)
1–2*	1·45	1·40	1·46	1·48	†	1·37	0·507
2–3	1·33	1·47	1·38	1·39	†	1·43	0·764
C–N	1·38	1·35	1·38	1·30	1·23–1·45	1·38	0·585
Bridge	1·38	1·43	1·37‡	1·29‡	1·32–1·48	†	0·523
N–metal	2·06	1·84	1·83	1·90	1·78–1·96	†	†

* Nomenclature is that of Fig. 3.

† Bond not even roughly comparable or non-existent.

‡ The bridge atom is nitrogen rather than carbon.

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References

BAK, B., CHRISTENSEN, D., HANSEN, L. & RASTRUP-ANDERSEN, J. (1956). *J. Chem. Phys.* **24**, 720.

BERGHUIS, J., HAANAPPEL, IJ.M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BUERGER, M. J. (1959). *Vector Space.* New York: Wiley.

BURNHAM, C. W. (1962). Paper B9, Amer. Cryst. Assoc. Annual Meeting, Villanova, Penna., June 1962.

COULSON, C. A. (1961). *Valence.* London: Oxford Univ. Press.

CRUTE, M. B. (1959). *Acta Cryst.* **12**, 24.

FALK, J. E., LEMBERG, R. & MORTON, R. K. (1961). *Haematin Enzymes.* Oxford: Pergamon Press.

FISCHER, H. (1941). In *Organic Syntheses,* **21**, 53. New York: Wiley.

FISCHER, H. & ORTH, H. (1937). *Die Chemie des Pyrrols, Pyrrolfarbstoffe,* II, Erste Halfte. Leipzig: Akademische Verlagsgesellschaft.

GANTZEL, P. K., SPARKS, R. & TRUEBLOOD, K. N. (1961). *Amer. Cryst. Assoc. Computer Program Listing,* 2nd Ed.

HAMILTON, W. C. (1955). *Acta Cryst.* **8**, 185.

HODGKIN, D. C., PICKWORTH, J., ROBERTSON, J. H., PROSEN, R. J., SPARKS, R. A. & TRUEBLOOD, K. N. (1959). *Proc. Roy. Soc.* A, **251**, 306.

HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.

KENDREW, J. C. (1963). *Science*, **139**, 1259.

LEMBERG, R. & LEGGE, J. W. (1949). *Hematin Compounds and Bile Pigments.* New York: Interscience.

LIPSON, H. & COCHRAN, W. (1957). *The Determination of Crystal Structures.* 2nd Ed. London: Bell.

MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.

PULLMAN, B. & PERAULT, A. M. (1959). *Proc. Nat. Acad. Sci. Wash.* **45**, 1476.

ROBERTSON, J. M. & WOODWARD, I. (1937). *J. Chem. Soc.* p. 219.

SPEAKMAN, J. C. (1953). *Acta Cryst.* **6**, 784.

WATSON, R. E. & FREEMAN, A. J. (1961). *Acta Cryst.* **14**, 27

Acta Cryst. (1965). **18**, 673

The Crystal Structure of a Polyiodide Complex with *N*-methylacetamide – $KI . KI_3 . 6(CH_3CONHCH_3)$

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The structure of $KI . KI_3 . 6(CH_3CONHCH_3)$ was determined. The crystals are trigonal, space group $P\bar{3}1c$, $a = 12{\cdot}2$, $c = 15{\cdot}2$ Å. The unit cell contains two stocichiometric units. Ions I^- and I_3^- alternate in arrays running parallel to the *c* axis. Cations K^+ occupy positions 000, 00¼, 00½, 00¾. NH groups of *N*-methylacetamide are linked to I^- ions, CO groups to K^+ cations. The presence of disorder in orientations of I_3^- ions is highly probable.

Introduction

The existence of complexes of polyamides with alkali polyiodides is well known (Kinoshita 1959, Arimoto 1962); their crystal structure, however, is still not very well understood. We suppose that one of the major difficulties here is the lack of information on the character of the bond between polyiodide and amide. It seemed therefore desirable to make a structure determination of a polyiodide complex with a low molecular weight amide. *N*-Methylacetamide was chosen, as here, according to Doskočilová & Schneider (1962), a greater tendency to formation of crystalline solvates with polyiodides was expected than in amides with a longer carbon chain.

Experimental

The solvate $KI . KI_3 . 6(CH_3CONHCH_3)$ was prepared as follows: 0·415 g potassium iodide, 0·317 g iodine and 1·1 g *N*-methylacetamide (molar ratios 1:0·5:6) were heated in a sealed glass tube at 100 °C for 8 hours. The tube containing the mixture was then slowly cooled for several hours to room temperature. In addition to a small quantity of potassium iodide, brownish-red needles of solvate crystallized from the mixture. The crystals of the complex were isolated in a dry box from the mother liquor. They are strongly hygroscopic; in moist air they disintegrate in a few minutes into a red liquid. The melting point of the brownish-red crystals is about 60 °C. The potassium