

The University of British Columbia

FACULTY OF GRADUATE STUDIES

PROGRAMME OF THE

FINAL ORAL EXAMINATION

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

of

CAROLYN SUSAN WILLISTON

B.Sc. (Hons), The University of British Columbia, 1964

TUESDAY, MAY 9th, 1967, AT 3:30 P.M.

IN ROOM 261, CHEMISTRY BUILDING

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Department of Chemistry

University of Alberta

Edmonton, Alberta

Research Supervisor: J. Trotter

ABSTRACT

Dimethyltellurium diiodide is known in two forms; the crystal structure of the β -form has been determined by X-ray diffraction. Mo-K α scintillation counter data were used for this analysis in which the heavy atoms were located from the Patterson function, the carbon atoms by a difference synthesis and refinement was by least-squares methods. β -dimethyltellurium diiodide is ionic, $[\text{Me}_3\text{Te}]^+ [\text{MeTeI}_4]^-$, and is built up from trigonal pyramidal Me_3Te^+ cations with $\text{Te} - \text{C} = 2.07 \text{ \AA}$, $\text{C} - \text{Te} - \text{C} = 95^\circ$, and square pyramidal MeTeI_4^- anions with $\text{Te} - \text{C} = 2.15 \text{ \AA}$, $\text{Te} - \text{I} = 2.84 - 2.98 \text{ \AA}$. The ions are bridged by four weak $\text{Te} \cdots \text{I}$ interactions (distances 3.84, 3.88, 3.97, 4.00 $\text{\AA}$), which complete a distorted octahedral environment around each tellurium atom.

The crystal and molecular structures of 2-biphenyl-ylferrocene and 4-biphenyl-ylferrocene have been investigated in order to compare the configuration of the rings of the biphenyl and ferrocene groups in these two molecules.

The structure of 2-biphenyl-ylferrocene has been determined with visual Cu-K α data. The iron atom position was found by Patterson methods, the carbon positions from successive Fourier summations. The positional and thermal parameters were refined by least-squares. The cyclopentadienyl rings are eclipsed, the first six-membered ring of the biphenyl-yl group is rotated 43° out of the cyclopentadienyl plane and the outer six-membered ring is rotated 58° out of the plane of the first six-membered ring. These rotations relieve the strain which would exist in a planar model for the $\text{C}_5\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_5$ group. The mean bond distances are $\text{Fe} - \text{C} = 2.05 \text{ \AA}$, $\text{C} - \text{C}$ (cyclopentadienyl) = $1.44 \text{ \AA}$.

Using Fe-K α scintillation counter data, the structure of 4-biphenyl-ylferrocene has been determined by Patterson

and Fourier methods and refined by least-squares. The two crystallographically independent molecules in the unit cell have slightly different conformations. In one the cyclopentadienyl rings are oriented about midway between the eclipsed and staggered conformations and the first six-membered ring is rotated 6° out of the plane of the cyclopentadienyl ring to which it is bonded, with the second six-membered ring rotated a further 9° . In the second molecule the cyclopentadienyl rings are only about 5° from the fully eclipsed position and the six-membered ring rotations are 0° and 10° . The mean bond distances are Fe-C = 2.07 Å, C-C (cyclopentadienyl) = 1.48 Å, C-C (biphenyl) = 1.43 Å, C-C (between rings) = 1.48 Å. The intermolecular separations correspond to van der Waals' interactions.

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PUBLICATIONS

Carolyn S. McCammon and James Trotter, THE STRUCTURE OF p-BROMOBENZOIC ANHYDRIDE, Acta Cryst., 17, 1333 (1964).

James Trotter and C.S. Williston, CRYSTALLOGRAPHIC STUDY OF AN UNKNOWN COMPOUND FROM WESTERN RED CEDAR, Acta Cryst., 20, 460 (1966).

James Trotter and C.S. Williston, BOND LENGTHS AND THERMAL VIBRATIONS IN m-DINITROBENZENE, Acta Cryst., 21, 285 (1966).

THE DETERMINATION OF THE CRYSTAL STRUCTURES OF
SOME INORGANIC COMPOUNDS BY
X-RAY DIFFRACTION

by

CAROLYN SUSAN WILLISTON

B.Sc. (Hon.), University of British Columbia, 1964

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

in the Department

of

Chemistry

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

April, 1967

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Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date May 9, 1967

ABSTRACT

Supervisor: Professor James Trotter

Dimethyltellurium diiodide is known in two forms; the crystal structure of the β -form has been determined by X-ray diffraction. Mo-K α scintillation counter data were used for this analysis in which the heavy atoms were located from the Patterson function, the carbon atoms by a difference synthesis and refinement was by least-squares methods. β -dimethyltellurium diiodide is ionic, $[\text{Me}_3\text{Te}]^+ [\text{MeTeI}_4]^-$, and is built up from trigonal pyramidal Me_3Te^+ cations with $\text{Te} - \text{C} = 2.07 \text{ \AA}$, $\text{C} - \text{Te} - \text{C} = 95^\circ$, and square pyramidal MeTeI_4^- anions with $\text{Te} - \text{C} = 2.15 \text{ \AA}$, $\text{Te} - \text{I} = 2.84 - 2.98 \text{ \AA}$. The ions are bridged by four weak $\text{Te} \cdots \text{I}$ interactions (distances 3.84, 3.88, 3.97, 4.00 $\text{\AA}$), which complete a distorted octahedral environment around each tellurium atom.

The crystal and molecular structures of 2-biphenyllylferrocene and 4-biphenyllylferrocene have been investigated in order to compare the configuration of the rings of the biphenyl and ferrocene groups in these two molecules.

The structure of 2-biphenyllylferrocene has been determined with visual Cu-K α data. The iron atom position was found by Patterson methods, the carbon positions from successive Fourier summations. The positional and thermal parameters were refined by least-squares. The cyclopentadienyl rings are eclipsed, the first six-membered ring of the biphenyl group is rotated 43° out of the cyclopentadienyl plane and the outer six-membered ring is rotated 58° out of the plane of the first six-membered ring. These rotations relieve the strain which would exist in a planar model for the $\text{C}_5\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_5$ group. The mean bond distances are $\text{Fe} - \text{C} = 2.05 \text{ \AA}$, $\text{C} - \text{C}$

(cyclopentadienyl) = 1.44 Å.

Using Fe- K_{α} scintillation counter data, the structure of 4-biphenylferrocene has been determined by Patterson and Fourier methods and refined by least-squares. The two crystallographically independent molecules in the unit cell have slightly different conformations. In one the cyclopentadienyl rings are oriented about midway between the eclipsed and staggered conformations and the first six-membered ring is rotated 6° out of the plane of the cyclopentadienyl ring to which it is bonded, with the second six-membered ring rotated a further 9°. In the second molecule the cyclopentadienyl rings are only about 5° from the fully eclipsed position and the six-membered ring rotations are 0° and 10°. The mean bond distances are Fe-C = 2.07 Å, C-C (cyclopentadienyl) = 1.48 Å, C-C (biphenyl) = 1.43 Å, C-C (between rings) = 1.48 Å. The intermolecular separations correspond to van der Waals' interactions.

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ACKNOWLEDGEMENTS

I wish to express my greatest appreciation for the inspiration and guidance Professor James Trotter has given me during the past four years. His ingenuity and personality have made working under his supervision a most rewarding and enjoyable experience.

My thanks are due to Dr. F. Einstein for the β -dimethyl-tellurium diiodide sample and for much helpful discussion and advice.

I am indebted to Dr. M.D. Rausch for the crystals of 2-biphenylferrocene and 4-biphenylferrocene.

Finally, I wish to thank the National Research Council of Canada for awarding me a Bursary for 1964-65 and Studentships for 1965-67.

GENERAL INTRODUCTION

Röntgen discovered X-rays in 1895. In 1912 von Laue suggested that a diffraction pattern should result from passing X-rays through a crystal and Friedrich and Knipping experimentally confirmed his theory. Bragg developed a mathematical interpretation of this phenomenon which, in 1913, enabled him to determine the first crystal structure by X-ray diffraction.

Before this time very little was known about the solid state. Properties which could be observed could not be explained. Knowledge of the behaviour of atoms and molecules in the liquid and gaseous states could be gained by observing chemical reactions. However, it was not even known what the basic unit of crystals was, although their general properties indicated a regular arrangement of small, identical units. But now a method was available to investigate the structure of crystals on an atomic scale.

Since 1913 the science of X-ray crystallography has developed rapidly and has been used to determine the crystal structures of thousands of compounds. These structures, of course, have made a primary contribution to the modern theories of structural inorganic chemistry.

Atoms attain their particular arrangement in the crystal because the various attractive and repulsive forces acting on them are in balance. An X-ray crystal structure determines the position of each atom in the unit cell and the distances between the atoms. Also the contoured electron density maps give an idea of atomic radii and how electrons may be spread out between atoms. This information of bond lengths and angles and electron distribution enables the inorganic chemist to deduce theories as to what type of bonding and other forces are present in the crystal. A complete X-ray analysis can indicate whether the bonding is primarily covalent or

primarily ionic, whether a compound actually exists as discrete molecules as in a simple covalent compound or whether it is completely ionic as in NaCl where there is coordination but no molecule. The crystal structure also suggests what the influence of intermolecular or interionic forces may be on the shape of a molecule or ion and shows any bridging interactions which may be present. Depending on whether the structure falls into the expected pattern or whether it has some unusual features, certain predictions can be made about related unknown compounds.

Thus, the structural information made available through the method of X-ray crystallography and from other methods has enabled the development of an extensive theory of the chemical bond.

With the modern automated X-ray equipment and growing computing facilities the number and the accuracy of structural determinations will continue to increase. And a greater understanding of the nature of molecules and crystals should be possible in the future.

This thesis is concerned with the determination by single-crystal X-ray diffraction of the structures of three inorganic compounds. These structures have been solved by Patterson and Fourier techniques and refined by least-squares methods which are described in many reference books including those listed in the Bibliography 1,2 and 3. All calculations were done on the IBM 7040 computer at the University of British Columbia Computing Centre.

Part I of the thesis describes the structure analysis of β -dimethyl-tellurium diiodide. Part II consists of the investigation of the crystal and molecular structures of two arylferrocenes, 2-biphenylferrocene and 4-biphenylferrocene.

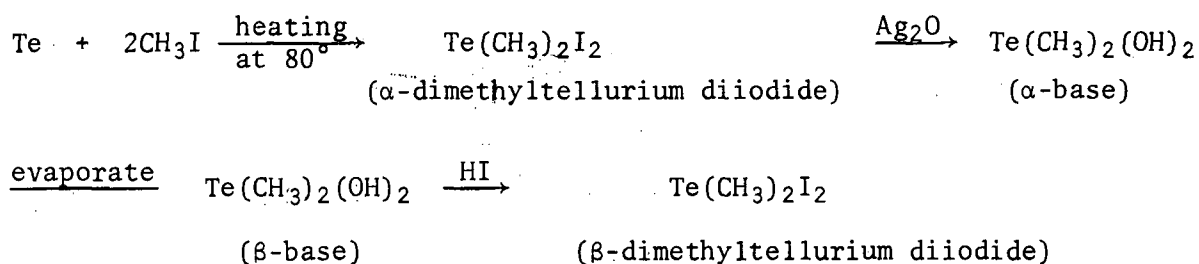
In Appendix I two computer programs written for special purposes in these analyses are described and listed. Appendix II contains the tables of observed and calculated structure factors of all compounds in the thesis.

PART I

THE DETERMINATION OF THE STRUCTURE OF
 β -DIMETHYLTELLURIUM DIIODIDE

A. INTRODUCTION

Vernon (4), in 1920, discovered that dimethyltellurium diiodide exists in two forms. He obtained these according to the following reactions postulating that they were trans and cis isomers of a square-planar structure.



However, Drew (5), in 1929, re-examined the diiodides and suggested that the α -dimethyltellurium diiodide had the covalent structure Me_2TeI_2 , but the β -compound was not isomeric, rather it was a complex salt-like compound. He showed that Vernon's β -diiodide can be made by mixing trimethyltellurium iodide (Me_3TeI) and methyltellurium triiodide (MeTeI_3). Also, reaction of potassium iodide with the β -diiodide gave Me_3TeI and $\text{K}[\text{MeTeI}_4]$. From this evidence Drew concluded that the β -compound was probably of the form $[\text{Me}_3\text{Te}]^+[\text{MeTeI}_4]^-$.

The crystals of β -dimethyltellurium diiodide used in this analysis were prepared by Dr. F. Einstein using Vernon's method (4) starting from a commercial sample of α -diiodide. They were shiny black plates without the strong odour of the red α -dimethyltellurium diiodide crystals.

Comparison of the mass spectra (6) of the α and β -diiodides showed that a peak corresponding to a Me_2TeI fragment that was present in the spectrum of the α -form was absent in that of the β -form. This would indicate that although the α -form could be simply Me_2TeI_2 the β -form probably does not contain a Me_2TeI unit.

Therefore, from the chemical and physical evidence it seemed likely

that β -dimethyltellurium diiodide would exist as $[\text{Me}_3\text{Te}]^+[\text{MeTeI}_4]^-$. On the basis of electron-pair repulsion theory (7) the cation, Me_3Te^+ , with three bonding pairs of electrons around the tellurium atom would be expected to assume a trigonal pyramidal structure. The lone pair would occupy the fourth position of a tetrahedron. The anion, MeTeI_4^- , has five bonding pairs and one lone pair of electrons surrounding the tellurium atom. Thus, it should exist as a square plane of iodine atoms around the tellurium atom with the methyl group above and the lone pair below the plane. It was interesting to determine whether this was the structure and to investigate the extent of interionic interactions which might occur.

Vernon (8) made an optical crystallographic comparison of the two diiodides. The results of his measurements were as follows: α -diiodide-monoclinic, $a:b:c = 0.5578:1:0.4310$, $\beta = 70^\circ 21'$; β -diiodide - monoclinic $a:b:c = 0.5465:1:0.4222$, $\beta = 76^\circ 52'$. Preliminary X-ray studies of $\alpha\text{-Me}_2\text{TeI}_2$ have been made by Galloni and Pugliese (9). Their cell constants are similar to those obtained from our crystals of $\alpha\text{-Me}_2\text{TeI}_2$ and to Vernon's data.

B. THE STRUCTURE OF β -DIMETHYLTELLURIUM DIIODIDE

Experimental

Crystals of β -dimethyltellurium diiodide are shiny black plates elongated along $\underline{c}$ with (010) developed. The unit cell and space group were determined from precession photographs and on the G.E. Spectrogoniometer. The density was measured by flotation in a solution of iodoform in methylene iodide.

Crystal data (λ , Mo- $\underline{K}_{\alpha}$ = 0.7107 Å)

β -dimethyltellurium diiodide, $[\text{Me}_3\text{Te}]^+[\text{MeTeI}_4]^-$; M.W. = 823.0.

Monoclinic, $\underline{a}$ = 8.12 ± 0.01 , $\underline{b}$ = 19.30 ± 0.02 , $\underline{c}$ = 10.58 ± 0.02 Å,

β = $103^\circ 15' \pm 5'$.

$\underline{U}$ = 1614 Å^3 , $\underline{D}_m$ = 3.5 g.cm.^{-3} , $\underline{Z}$ = 4 (i.e. 8 Me_2TeI_2 units), $\underline{D}_x$ = 3.4 g.cm.^{-3} .

$\underline{F}(000)$ = 1408.

Absorption coefficient for X-rays, $\mu(\text{Mo-}\underline{K}_{\alpha})$ = 114 cm.^{-1} .

Absent reflexions: $\underline{h}0\underline{l}$ when $\underline{l}$ is odd, $0\underline{k}0$ when $\underline{k}$ is odd. Space group is $\underline{P}2_1/\underline{c}(\underline{C}2_h^5)$.

The axial ratios and angle ($\underline{a}:\underline{b}:\underline{c}$ = 0.4210:1:0.5483; β = 103.3°) are in agreement with those measured optically (0.4222:1:0.5465; 103.1°).

The intensities of the reflexions were measured on a General Electric XRD 5 Spectrogoniometer with Single Crystal Orienter, using a scintillation counter, approximately monochromatic Mo- $\underline{K}_{\alpha}$ radiation (zirconium filter and pulse height analyser), and a θ - 2θ scan. Of 1504 reflexions with $2\theta(\text{Mo-}\underline{K}_{\alpha}) \leq 40^\circ$ (corresponding to a minimum interplanar spacing of 1.04 Å), 1213 were observed. The 291 unobserved reflexions were included in the analysis with $|\underline{F}_o| = 0.6 \underline{F}_{\text{threshold}}$. All the intensities were corrected for background (approximately a function of θ only). The crystal measured

0.42 x 0.10 x 0.75 $\pm$ 0.03 mm. along a, b, and c respectively and was mounted with c* parallel to the ϕ axis of the goniostat. Absorption was serious and corrections were applied by the method of Zalkin, Forrester and Templeton (10) (see Appendix I:A);

$$I(\text{corrected}) = I(\text{measured}) / \{1 + 9.35 \exp(-0.63/\underline{m})\}.$$

The correction factor varied from 0.168 to 1.000. Lorentz and polarization factors were applied and the structure amplitudes were derived.

Structure Analysis

The positions of the four iodine atoms and two tellurium atoms were determined from the three-dimensional Patterson function by considering the predicted structure, $[\text{Me}_3\text{Te}]^+[\text{MeTeI}_4]^-$. A square plane of iodine atoms was chosen from the strong near origin peaks so that I(1) and I(3), I(2) and I(4) were related by a centre of symmetry at the origin. Thus, iodine coordinates were obtained relative to the central tellurium atom at the origin. The six peaks on the Harker line at (0, $\frac{1}{2}$, $\frac{1}{2}$) and the eight peaks on the Harker section at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) were then examined to find (x, y, z) coordinates consistent with the relative coordinates. This was aided by the realization that the strongest peak on the Patterson map, other than the origin peak, was the ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) Te(5) - Te(5)' peak because it also included I(1) - I(3)', I(2) - I(4)', I(3) - I(1)' and I(4) - I(2)' peaks due to the symmetry of the square plane. After the Harker peaks for the four iodine atoms and the central tellurium atom were assigned, there were three remaining peaks on the Harker section, one of which, together with the sixth peak on the Harker line, determined the coordinates of Te(6). All of the major peaks on the Patterson map could be explained by the atomic coordinates chosen, which were all within 0.3 Å of their final values.

Structure factors were calculated using scattering factors from the International Tables for X-ray Crystallography (11) and with $B = 3.0 \text{ \AA}^2$ for all six atoms, giving an R factor of 0.41. The positional and isotropic thermal parameters were then refined by block-diagonal least-squares methods. The function minimized was $\sum w(F_o - F_c)^2$, with $\sqrt{w} = 0.35$ for unobserved reflexions, $\sqrt{w} = 1$ when $|F_o| \leq 80$, and $\sqrt{w} = 80/|F_o|$ when $|F_o| > 80$, so that the average $w(F_o - F_c)^2$ was approximately constant over all values of F_o taken at intervals of 20. Two cycles of least-squares reduced R to 0.19.

Refinement was continued for several more cycles, then a $(F_o - F_{Te,I})$ difference synthesis was computed to locate the four carbon atoms. The largest peaks (up to $6.5 \text{ e.\AA}^{-3}$) on the difference map occurred in the regions of the heavy atom positions indicating the presence of absorption and perhaps anisotropic thermal motion. The carbons were placed, partly from stereochemical considerations, on peaks of 5.6, 5.8, 5.2, $4.3 \text{ e.\AA}^{-3}$ for C(7), C(8), C(9) and C(10) respectively. These carbon atoms, with $B = 4.5 \text{ \AA}^2$, were included in the next structure factor calculations. Refinement of the parameters of all ten atoms proceeded until R was 0.17. The small shifts for the carbon atoms indicated they had been placed correctly.

At this point, an examination of the values of F_o , F_c and the absorption correction for each reflexion suggested that the correction was too severe. The intensities were then recorrected according to the equation

$$I(\text{corrected}) = I(\text{measured}) / \{1 + 6.50 \exp(-0.68/m)\}$$

so that the graph of F_o/F_c versus the absorption correction was approximately a line of zero slope. The new correction factor varied from 0.235 to 1.000. A structure factor calculation using the recorrected data gave $R = 0.15$. Further refinement with isotropic thermal parameters reduced R

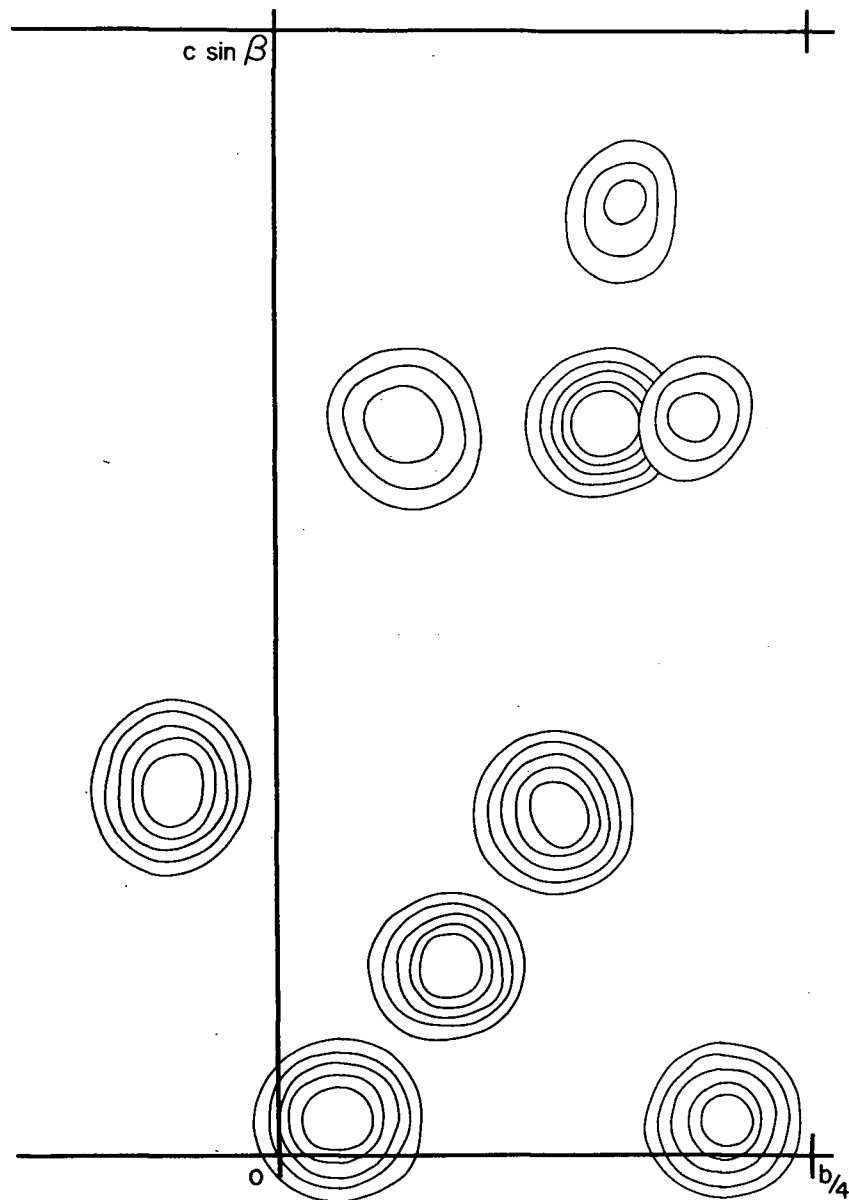
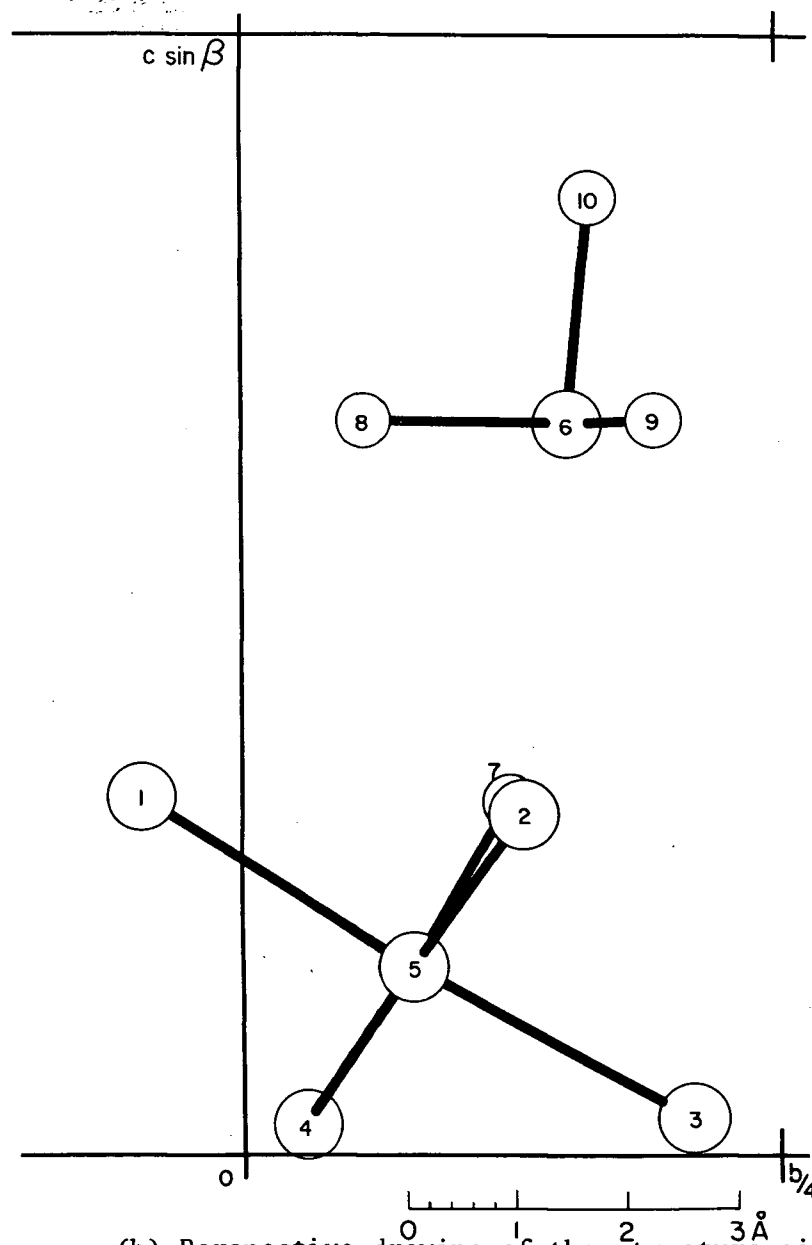


Figure 1. (a) Electron-density projection along the a axis. Contours are at intervals of $1 \text{ e. \AA}^{-3}$, starting at $2 \text{ e. \AA}^{-3}$ for C, and of $10 \text{ e. \AA}^{-3}$ starting at $10 \text{ e. \AA}^{-3}$ for Te and I.



(b) Perspective drawing of the structure giving the numbering used.

to 0.12, and refinement with anisotropic thermal parameters for the tellurium and iodine atoms gave $R = 0.09$. At this stage, the corresponding discrepancy factors for the uncorrected and over-corrected data were 0.19 and 0.12, so that the corrections for absorption improved the structure factor agreement considerably. Analysis of the values of $w(F_o - F_c)^2$ suggested alteration of $\sqrt{w}$ for the observed reflexions to $1/[1 + \{(|F_o| - 50)/40\}^2]^{1/2}$; in addition the three most intense reflexions (300, $\bar{1}22$, 150), which were apparently affected by extinction, were removed. Further refinement then produced negligible changes in the parameters.

The final measured and calculated structure factors are listed in Table VII (Appendix II), ($R = 0.09$ for the 1213 observed reflexions). A final three-dimensional Fourier series was summed and superimposed sections of the resulting electron-density distribution are shown in Figure 1, together with a drawing of the structure giving the atom numbering used in the analysis. A final difference map showed maximum fluctuations of $\pm 2 \text{ e.}\text{\AA}^{-3}$.

Coordinates and Molecular Dimensions

The final positional and thermal parameters are given in Table I. x , y and z are fractional coordinates referred to the monoclinic crystal axes and U_{ij} are the components of the vibration tensors, written in matrix form and referred to axes a^* , b^* and c^* . Table I also gives the magnitudes of the principal axes of the vibration ellipsoids, which are not physically unreasonable, the vibrations being smallest along the bonds. The significant interatomic distances and angles are given in Table II.

The mean plane through the four iodine atoms in the MeTeI_4^- ion has the equation:

Table I.

Final positional parameters (fractional) and standard deviations ($\text{\AA}$), and thermal parameters and standard deviations (U_{ij} in $\text{\AA}^2 \times 10^2$; B in $\text{\AA}^2$)

Atom	<u>x</u>	<u>y</u>	<u>z</u>	Mean $\sigma(\text{\AA})$
I(1)	0.0788	-0.0479	0.3215	0.0053
I(2)	0.3752	0.1322	0.3017	0.0057
I(3)	-0.0388	0.2109	0.0303	0.0059
I(4)	-0.2854	0.0299	0.0298	0.0053
Te(5)	0.0334	0.0808	0.1673	0.0041
Te(6)	0.3344	0.1550	0.6538	0.0053
C(7)	-0.0742	0.1266	0.3150	0.065
C(8)	0.4251	0.0582	0.6557	0.069
C(9)	0.5730	0.4955	0.6586	0.087
C(10)	0.3458	0.1658	0.8557	0.086

Atom	<u>U</u> ₁₁	<u>U</u> ₁₂	<u>U</u> ₁₃	<u>U</u> ₂₂	<u>U</u> ₂₃	<u>U</u> ₃₃	Mean $\sigma(\text{\AA})$
I(1)	6.1	0.6	2.4	5.2	1.2	9.3	0.3
I(2)	5.6	-1.5	1.0	5.6	-0.9	9.6	0.3
I(3)	9.4	-0.9	2.3	5.1	1.9	10.3	0.3
I(4)	5.6	-1.6	0.6	6.6	-0.1	6.5	0.3
Te(5)	4.7	-0.8	1.8	3.5	-0.8	5.7	0.2
Te(6)	5.9	2.3	2.7	5.6	1.9	9.6	0.3

Atom	<u>B</u>	$\sigma(\text{\AA})$
C(7)	3.7	1.3
C(8)	4.1	1.4
C(9)	6.2	1.9
C(10)	6.1	1.9

Magnitudes of principal axes of vibration ellipsoids:

Atom	<u>U'</u> ₁₁	<u>U'</u> ₂₂	<u>U'</u> ₃₃
I(1)	4.8	5.8	9.7
I(2)	4.1	7.1	10.1
I(3)	4.2	9.6	11.1
I(4)	4.3	6.6	8.1
Te(5)	3.0	4.3	6.2
Te(6)	3.5	6.6	10.7

$$-0.584 \bar{x}' + 0.397 \bar{y} + 0.708 \bar{z}' = 1.963,$$

where $\bar{x}'$, $\bar{y}$ and $\bar{z}'$ are in Å and referred to orthogonal axes $\underline{a}$, $\underline{b}$ and $\underline{c}^*$. The displacements from this plane of the I(1), I(2), I(3), I(4) and Te(5) atoms are -0.10, + 0.10, -0.10, + 0.12 and + 0.04 Å respectively, so that the iodine atoms are alternately slightly above and below the plane, the displacements being highly significant.

Discussion

This crystal structure analysis has shown β -dimethyltellurium diiodide to be a coordinate compound consisting of the Me_3Te^+ ion and the MeTeI_4^- ion. However, a number of relatively short interionic I...Te contacts is evidence of some bridging interactions.

The cation, Me_3Te^+ , has a distorted trigonal pyramidal structure. Or it could be considered as tetrahedral with the lone pair occupying the fourth position. This is the structure expected for sp^3 hybridization of the tellurium atomic orbitals. The average C-Te-C angle is 95° ($\sigma = 2^\circ$). The repulsion from the lone pair would tend to reduce the angle relative to the regular tetrahedral angle of 109.5° . It can be compared to the following bond angles (12): OMe_2 - 110° ; OH_2 - 104.5° ; TeH_2 - 89.5° . The small angle at Te relative to that at O can be explained by the fact that Te is larger and less electronegative than O and thus the bonding pairs are drawn further out towards H and further apart from each other, and the bond-pair: bond-pair repulsion is less. This can also be considered as an increase in p character of the bond as the electron pairs are drawn out from the nucleus. However, in TeMe_3^+ an angle larger than 89.5° is expected because of the size of the three methyl groups and because of the presence of only one lone pair instead of the two in TeH_2 . The average Te-C bond length is 2.07 Å ($\sigma = 0.06$ Å)

Table II.

Interatomic distances(Å) and angles (degrees)

[MeTeI ₄] ⁻		[Me ₃ Te] ⁺	
Te(5) - C(7)	2.15	Te(6) - C(8)	2.01
		Te(6) - C(9)	2.08
		Te(6) - C(10)	2.13
Te(5)...I(4) ^I	3.88	mean	2.07
Te(5) - I(1)	2.948	Te(6)...I(1) ^{II}	4.00
Te(5) - I(2)	2.984	Te(6)...I(2)	3.84
Te(5) - I(3)	2.891	Te(6)...I(3) ^{III}	3.97
Te(5) - I(4)	2.840		
I - Te(5) - I	88.6, 89.3, 90.6	C - Te(6) - C	91, 97, 99
	91.8, mean 90.0		mean 95
I - Te(5) - C	87, 88, 90, 92	C - Te(6)...I	77-114(cis)
			149, 170, 173(trans)
C(7) - Te(5)...I(4) ^I	166		
I - Te(5)...I(4) ^I	80-106		

Standard deviations

Te - I 0.007

Te - C 0.08

I - Te - I 0.2

I - Te - C 1.7

C - Te - C 3.2

Equivalent positions

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

compared to 2.09 Å in α -Me₂TeCl₂ (13).

The anion, MeTeI₄⁻, is a distorted square pyramid. This structure can be explained by d^2sp^3 hybridization of the tellurium orbitals, the lone pair occupying the sixth position of the octahedron opposite the methyl group. The iodine atoms are alternately above and below their mean plane by 0.1 Å, the C-Te-I angles averaging 87° and 91°. This buckling is probably caused by steric interactions between the iodines, the mean I...I distance being 4.13 Å. The Te-C bond distance is 2.15 Å. The Te-I bond lengths are 2.84, 2.89, 2.95 and 2.98 Å; these are of the same order as those in (p-ClC₆H₄)₂TeI₂ (2.92 and 2.95 Å) (14), but the differences between the four bond lengths are highly significant and are probably related to the involvement of the iodines in interionic interactions.

The structure contains four short interionic Te...I distances of 3.84, 3.88, 3.97, 4.00 Å (Table II, Figures 1 and 2). The sum of the van der Waals' radii of tellurium and iodine is 4.35 Å (15). All the other interionic distances are greater than the sums of the van der Waals' radii, the shortest contacts being Te...I = 4.38 Å, I...I = 4.43 Å, I...C = 3.85 Å. The four relatively short contacts suggest weak bridge-bonding between the ions.

Three of these contacts are from the Me₃Te⁺ cation to three different iodines of three neighbouring MeTeI₄⁻ anions and these contacts complete a distorted octahedral environment around the tellurium atom of the Me₃Te⁺ ion. The lone pair on this tellurium atom would be in the centre of the three iodine contacts. The distances and angles in the bridges may be summarized as follows:

	Te(5) - I	I...Te(6)	I...Te(6) - C
I(1)	2.95 Å	4.00 Å	170°
I(2)	2.98	3.84	173
I(3)	2.89	3.97	149

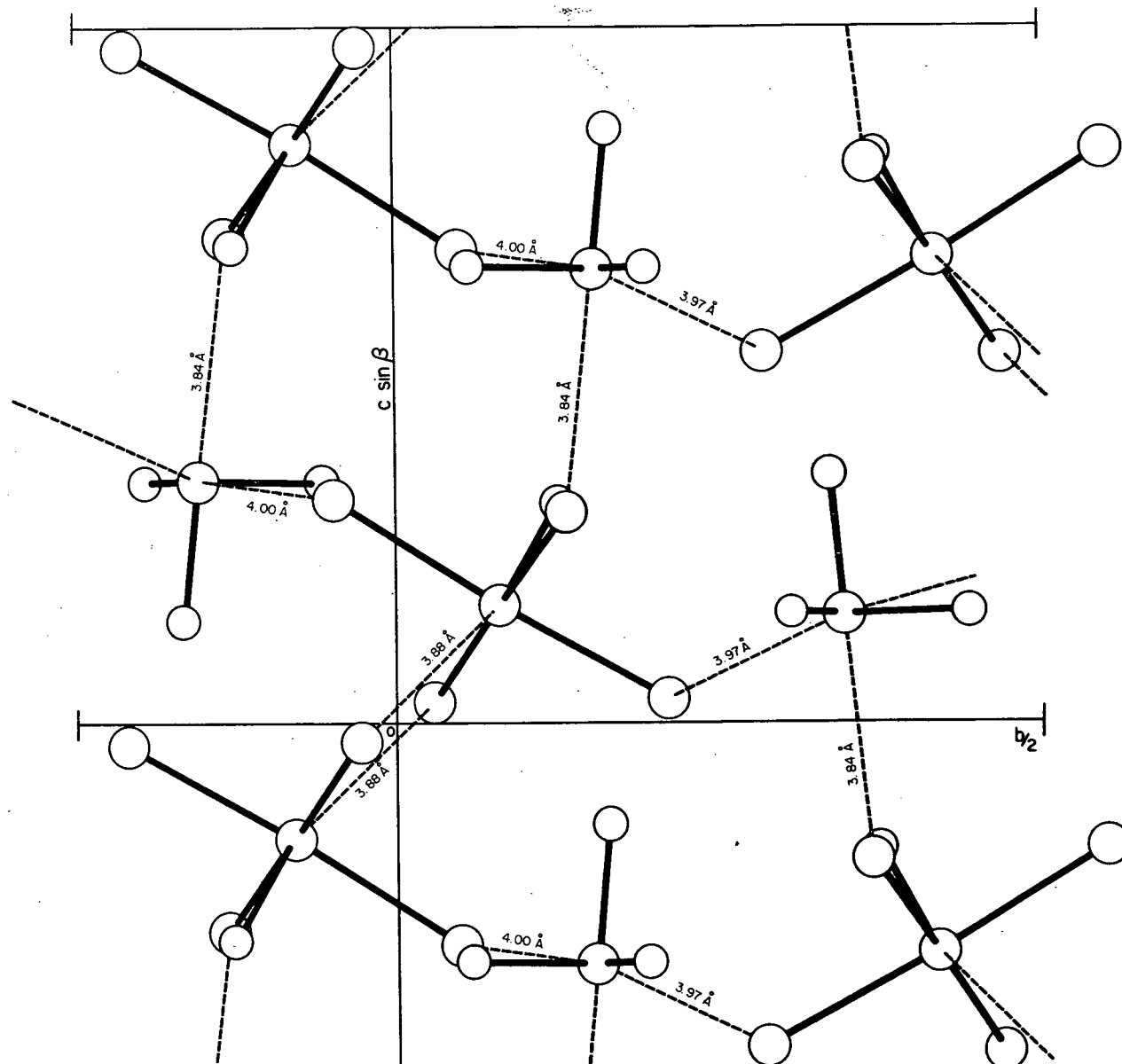


Figure 2. View of the structure along a , illustrating the packing of the ions and giving the short interionic Te...I distances.

0 1 2 3 Å

where the trans I...Te-C angles are listed. The greatest deviation of these angles from the regular octahedral value of 180° is for the contact involving I(3), 149° , and this contact is one of the longer and presumably weaker bridges, $3.97 \text{ \AA}$. The Te-I(3) bond distance is the shortest of the three. I(2) is involved in the shortest and most regular contact, $3.84 \text{ \AA}$ and 173° , and in the longest Te-I bond. I(1) is approximately intermediate. The Te-I...Te angles at I(1), I(2) and I(3) are 118° , 103° and 110° respectively. The forces involved in these bridging interactions are probably largely electrostatic. However, there may be some donation of electrons from iodine to d-orbitals on the tellurium atom, resulting in partial neutralization of the positive charge on the cation.

The fourth short interionic Te...I distance, $3.88 \text{ \AA}$, occurs between MeTeI_4^- anions, these anions being joined by two such contacts to form centrosymmetrical dimers (Figure 2). The Te(5)-I(4) bond distance, $2.84 \text{ \AA}$, is the shortest of the four Te-I lengths and the Te(5)...I(4) interionic contact, $3.88 \text{ \AA}$, is also one of the shorter interionic distances. The Te-I(4)...Te angle is 86° . This bridging occurs to the region where the lone pair electrons of the tellurium atom are expected to be, the C-Te...I angle being 166° . Therefore, the interionic bonding in the anion likely involves donation of electrons from the tellurium lone pair into d-orbitals of the iodine atom. This is in contrast to the cation in which the positive charge means its non-bonding lone pair is influenced by a relatively strong field and as a result does not appear to be directly involved in the bonding. On the other hand, the lone pair on the negatively charged anion is more weakly held and is more available for interionic bonding.

Thus the structure of β -dimethyltellurium diiodide consists essentially of trigonal pyramidal Me_3Te^+ cations and square pyramidal MeTeI_4^- anions. The interionic bridge-bonds which occur indicate that it cannot be regarded

as a purely ionic compound.

PART II

THE DETERMINATION OF THE STRUCTURES OF

2-BIPHENYLYL FERROCENE

AND

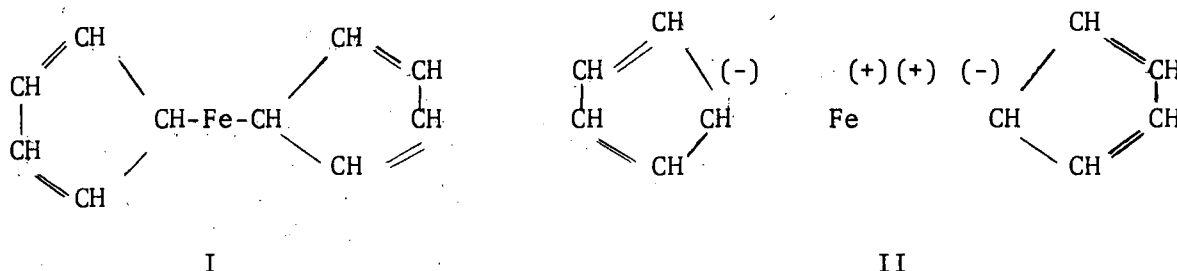
4-BIPHENYLYL FERROCENE

A. INTRODUCTION

Both 2-biphenylferrocene and 4-biphenylferrocene consist of a biphenyl ligand attached to ferrocene. The structures of biphenyl and of ferrocene in the solid and in the vapour states have been studied because the configurations they assume are important in relation to possible explanations of bonding in these compounds. It was of interest to determine the crystal structures of 2-biphenylferrocene and 4-biphenylferrocene to compare the orientations of the biphenyl rings and the arrangement of the cyclopentadienyl rings with those of biphenyl and ferrocene. These structures analyses should provide further evidence as to the relative importance of intermolecular packing forces and intramolecular bonding forces in determining the orientations of the molecules.

Electron diffraction studies (16) indicated that in the vapour the angle between the planes of the two rings of biphenyl was 45° . However, X-ray analyses (17) showed that biphenyl was almost completely planar in the solid state. Even the ortho hydrogens which would be expected to be pushed out of the molecular plane by steric repulsion, remained in the plane. The distance between them was increased from $1.80 \text{ \AA}$ to $2.07 \text{ \AA}$ by the opening of the C-C-H valency angle from 120° , thus relieving the strain without sacrificing planarity. However, because of the long inter-ring C-C bond length and its non-planarity in the vapour state, it seems unlikely that there is much delocalization of electrons between the two rings but rather it is intermolecular packing forces which are the main cause of biphenyl's planarity in the crystalline state. It is quite possible then, that under the different packing forces experienced in the 2-biphenylferrocene and 4-biphenylferrocene molecules the strain of the ortho hydrogens would cause the rings to be rotated from a coplanar position.

Dicyclopentadienyl iron (first written as I) was discovered accidentally in 1951 (18). To explain its remarkable stability it was proposed that there were important contributions from the resonance form (II) and intermediates and the cyclopentadienyl group tends to become "aromatic".



This compound's unusual character and structure created great interest and further chemical and physical investigations immediately followed. The X-ray analysis (19) showed its structure to consist of the iron atom sandwiched between two parallel cyclopentadienyl rings. Various theories were put forth to explain the bonding. These theories had to allow for the experimentally observed features of equivalent bonding to all five carbons in each ring and free rotation of the rings, which had been shown to occur in the vapour (20).

The two cyclopentadienyl rings in ferrocene are staggered (19) as they are in the corresponding Co(21), Ni(21), V(22) and Cr(22) compounds. However, in ruthenocene (23) and osmocene (24) the rings are in the eclipsed configuration. This suggests that it is probably lattice forces, rather than the metal-ring bonding forces, which determine the ring orientations. Although, possibly the fact that the rings in ruthenocene (inter-ring distance 3.68 Å (23)) are further apart than in ferrocene (inter-ring distance 3.32 Å (19)) could explain why the former compound more easily assumes an eclipsed configuration, when the staggered one would be expected to be more stable. However, ferrocene, biferrocenyl (25) and differocenyl ketone (26)

have inter-ring distances of 3.32 Å, 3.32 Å and 3.30 Å respectively, yet, whereas the rings in ferrocene are staggered (36° rotation from eclipsed position), those in biferrocenyl are rotated 17° and the rings in differocenyl are rotated only 5.2° from an eclipsed position. This further indicates that the packing forces are most important in determining the rotational configuration of the cyclopentadienyl rings.

It is also interesting that the cyclopentadienyl rings in these compounds are not always parallel. Although the rings in ferrocene are essentially parallel, those in 1,1'-tetramethylene-ferrocene (27), for example, are tilted 23° with respect to one another.

2-biphenylylferrocene and 4-biphenylylferrocene were prepared by Dr. M.D. Rausch (28) by simultaneous decomposition of differocenylmercury and the corresponding di-biphenylylmercury compound in the presence of silver. He also synthesized 4-biphenylylferrocene by reaction of 4-biphenylyldiazonium chloride and ferrocene.

B. THE STRUCTURE OF 2-BIPHENYLYLFERROCENE

Experimental

Crystals of 2-biphenylferrocene (28) are orange-yellow needles elongated along b. The density was measured by flotation in aqueous potassium iodide and the unit cell dimensions and space group were determined from rotation and Weissenberg photographs.

Crystal data (λ , Cu-K $_{\alpha}$ = 1.5418 Å)

2-Biphenylferrocene, C₂₂H₁₈Fe; M.W. = 338.2; m.p.=133-134°.

Orthorhombic, a = 23.16, b = 5.92, c = 11.56 Å.

U = 1585 Å³, D_m = 1.40, Z = 4, D_x = 1.42 g.cm.⁻³.

F(000) = 704.

Absorption coefficient for X-rays, $\mu(\text{Cu-K}_{\alpha}) = 77 \text{ cm.}^{-1}$

Absent reflexions: Ok ℓ when ℓ is odd, h0 ℓ when h is odd. Space group is Pca2₁ (C_{2v}⁵) or Pcam (D_{2h}¹¹). Pca2₁ from structure analysis.

All the crystals were very small and poorly formed and gave poor diffraction patterns which exhibited a rapid decrease in intensity with increasing Bragg angle. Nevertheless, interest in the general structure of the molecule prompted the continuation of the analysis, although the paucity of experimental data precluded the accurate measurement of bond distances. The best diffraction patterns were obtained with Cu-K $_{\alpha}$ radiation, which was therefore used in preference to molybdenum or iron radiations. The intensities of the reflexions were estimated visually from hK ℓ Weissenberg films (K = 0 $\rightarrow$ 3); only 313 reflexions were observed. The crystal used had cross-section 0.05 x 0.05 mm., so that absorption errors were not serious and no corrections were applied. Lorentz and polarization corrections were made and the structure amplitudes were derived. The scale factors between

the layers were initially estimated by timing the exposures and were later adjusted slightly from comparisons of measured and calculated structure factors.

Structure Analysis

A preliminary study was made of the two-dimensional $h0l$ projection. The Fe-Fe peaks in the Patterson function implied Fe coordinates of either (0.15, 0) or (1/4-0.15,0), the two positions giving the same vector map. From the Fourier synthesis summed with phases based on the iron atom only, a possible molecular outline could be distinguished which indicated that the mirror plane which occurred at $z = 0$ was spurious. When the twenty-two carbon atoms were approximately located and structure factors then calculated using Fe and C scattering factors of the International Tables for X-ray Crystallography (11) with $B = 6.0 \text{ \AA}^2$ for Fe and $B = 4.5 \text{ \AA}^2$ for C, the discrepancy index, R , was 0.26. Therefore, it was decided to continue the analysis in three-dimensions.

The three-dimensional Patterson could be interpreted in terms of space group P_{cam} with iron coordinates (0.15,0,0) or (1/4-0.15,0,0). Two three-dimensional electron-density distributions were computed with phases based on the two possible iron positions. The resulting maps had, of course, P_{cam} symmetry, but again the mirror plane was spurious (the mirror symmetry could have been retained by allowing a disordered arrangement of molecules, but at no stage in the analysis was there any evidence to suggest disorder). Both maps showed chemically reasonable molecules and revealed the positions of the seventeen carbon atoms in the biphenylcyclopentadienyl group, based on space group $P_{\text{ca}2_1}$. Since structure factor calculations gave $R = 0.30$ and 0.34 for the two possible structures and also the first gave better

packing of the molecules in the unit cell, it seems to be the correct arrangement.

From the Fourier summed using the iron coordinates of (0.15,0,0) and the corresponding biphenylcyclopentadienyl carbon coordinates (i.e. the first structure), the other cyclopentadienyl ring carbon atoms could be unambiguously located.

Refinement of the positional and isotropic thermal parameters proceeded by block diagonal least-squares methods, minimizing

$\sum w(|F_o| - |F_c|)^2$, with $\sqrt{w} = |F_o|/50$ when $|F_o| < 50$ and $\sqrt{w} = 50/|F_o|$ when $|F_o| \geq 50$. The layer line scaling was adjusted by equating $\sum |F_o|$ and $\sum |F_c|$ for each layer after each least-squares cycle.

After several cycles of least-squares the R value was 0.19. Then, since the calculated structure factors corresponding to the more intense reflexions were consistently higher than the observed, these reflexions, (400, 600, 201, 202, 402, 602, 410, 211) were corrected for extinction before further refinement. This was done according to the empirical method of Pinnock, Taylor and Lipson (29) using equation

$$I_c/I_o = 1 + (g/\mu) I_c$$

where I_o is the observed intensity

I_c is the calculated intensity

μ is the absorption coefficient

g is a constant.

This procedure is regarding secondary extinction as equivalent to an increase in the absorption coefficient of each reflexion.

Refinement was continued until the shifts became small and were in random directions. The final R value was 0.15 for the 313 observed

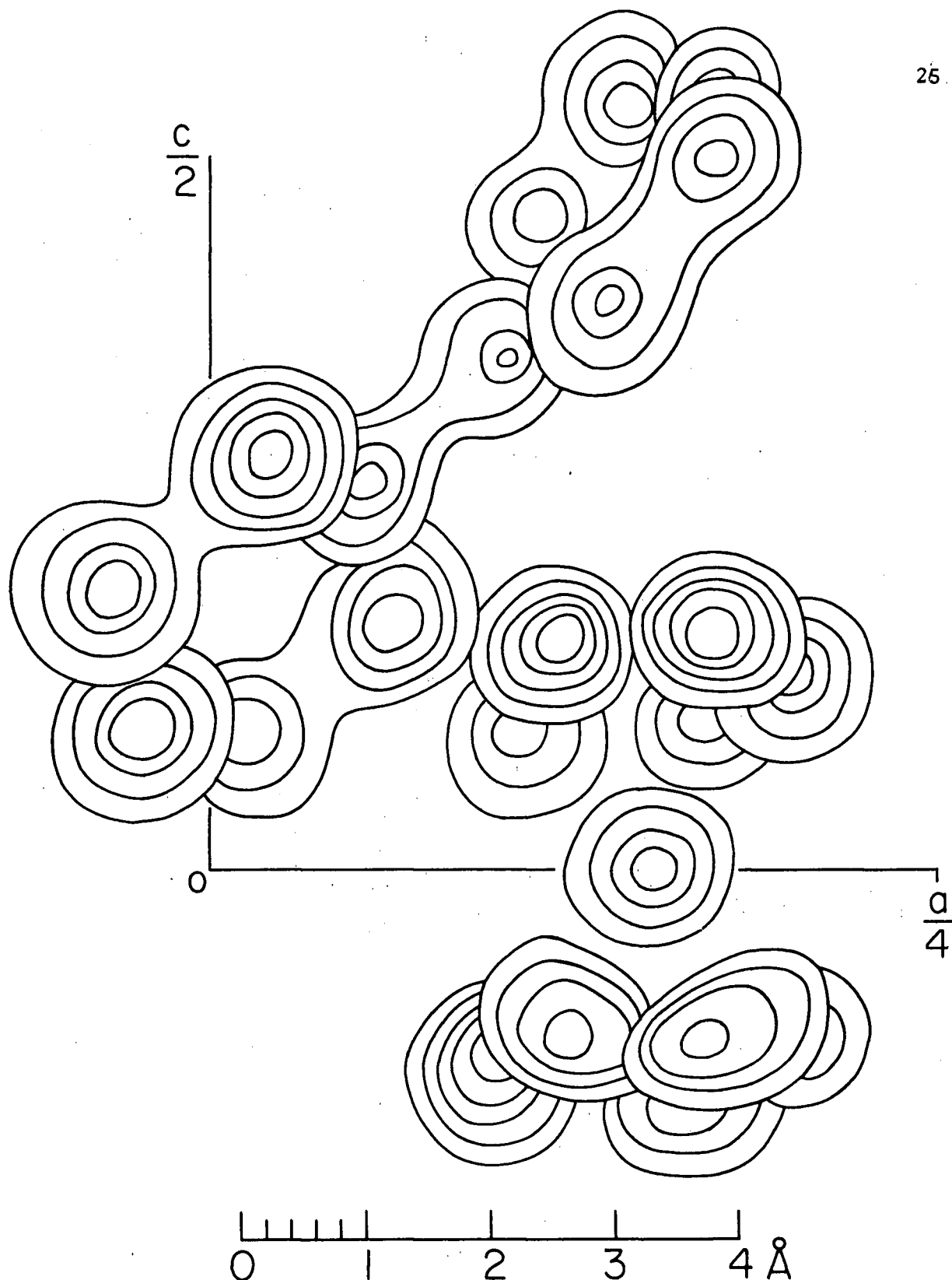


Figure 3. Superimposed sections of the three-dimensional electron-density distribution, through the atomic centres parallel to (010). Contours are at intervals of $0.7 \text{ e. \AA}^{-3}$, starting at $1.4 \text{ e. \AA}^{-3}$ for C, and $3.5 \text{ e. \AA}^{-3}$, starting at $7.0 \text{ e. \AA}^{-3}$ for Fe.

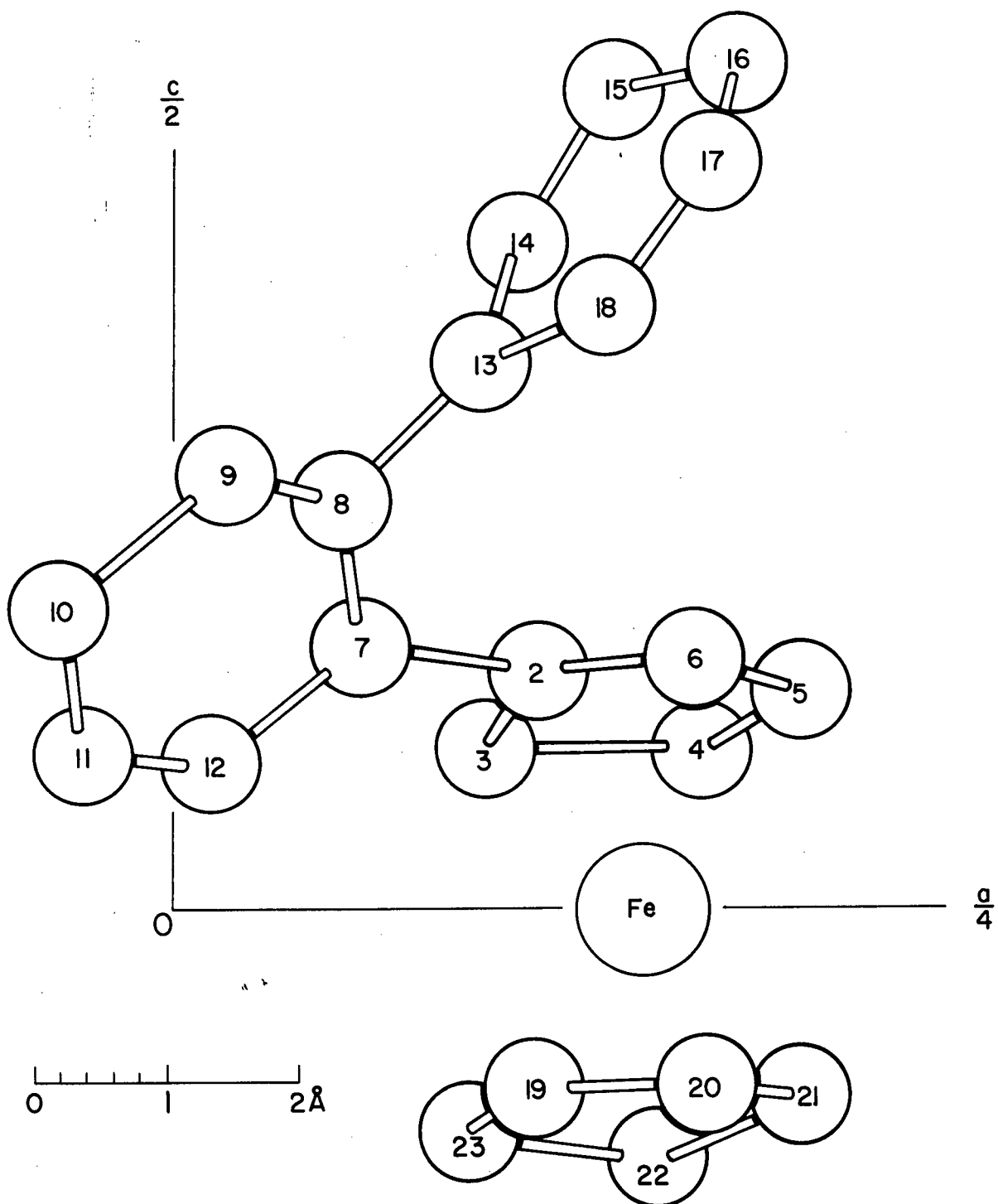


Figure 4. A perspective drawing of the molecule giving the atom numbering used.

reflexions. Measured and calculated structure factors are listed in Table VIII (Appendix II).

A final three-dimensional Fourier series was summed and superimposed sections of the resulting electron-density distribution are shown in Figure 3. Figure 4 is a drawing of the molecule giving the atom numbering used for convenience in the analysis. A final difference map showed no significant spurious detail, the maximum fluctuation being $\pm 0.6 \text{ e. \AA}^{-3}$.

Coordinates and Molecular Dimensions

The final positional and thermal parameters are given in Table III. The individual bond distances and angles are not very accurate ($\sigma \sim 0.07 \text{ \AA}$ and 5°), and the average values only are given in Table IV. Table IV also gives the equations of the mean planes of the various rings and the angles between the planes. All the intermolecular contacts correspond to van der Waals' interactions or greater, the shortest C...C distance being $3.3 \text{ \AA}$. The arrangement of the molecules in the crystal is shown in Figure 5.

Discussion

In the 2-biphenylferrocene molecule the iron atom is sandwiched between the two cyclopentadienyl rings. These rings appear to be not quite parallel, although the angle between the normals, 8° , is not really significantly different from zero. The three rings of the 2-biphenylcyclopentadienyl group exhibit large deviations from coplanarity which relieve the strain which would exist in a planar configuration. The cyclopentadienyl ring is rotated about the C(2)-C(7) bond 43° out of the plane of the $-\text{C}_6\text{H}_4-$ ring and the outer six-membered ring is rotated about the C(8)-C(13) bond by 58° from the $-\text{C}_6\text{H}_4-$ plane. The two rotations are in

Table III

Final positional (fractional $\times 10^3$) and thermal ($\text{\AA}^2$) parameters. Mean standard deviations are $\sigma(\underline{x}) = \sigma(\underline{y}) = \sigma(\underline{z}) = 0.009 \text{ \AA}$ for Fe, $0.05 \text{ \AA}$ for C; $\sigma(\underline{B}) = 0.2 \text{ \AA}^2$ for Fe, $1.5 \text{ \AA}^2$ for C.

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}$
Fe(1)	152.2	-029.7	0	6.8
C(2)	118	012	156	1.5
3	101	-203	105	4.8
4	172	-289	104	8.6
5	203	-106	143	3.5
6	169	066	167	1.7
7	060	135	173	2.4
8	053	299	265	4.2
9	016	499	286	2.0
10	-036	523	198	5.9
11	-028	358	102	4.5
12	010	155	095	5.2
13	098	294	358	3.7
14	108	084	430	8.3
15	142	112	538	5.7
16	182	333	550	6.7
17	174	515	488	7.9
18	139	529	392	5.7
19	118	195	-121	4.5
20	174	247	-121	6.2
21	203	061	-127	4.9
22	157	-135	-168	6.9
23	097	-038	-148	2.7

Table IV.

Mean bond distances ($\sigma \sim 0.07 \text{ \AA}$) and valency
 angles ($\sigma \sim 5^\circ$), equations of mean planes
 and angles between planes.

Distances and angles

Fe-C	2.05		
C-C(5-rings)	1.44	C-C-C(5-rings)	108
C-C(6-rings)	1.50	C-C-C(6-rings)	120
C-C(between rings)	1.52		

Equations of mean planes, in the form $\ell X' + mY + nZ' + p = 0$,
 where X', Y, Z' are coordinates in A referred to orthogonal
 axes $\underline{a}, \underline{b}, \underline{c}^*$.

Plane	Atoms	$\underline{\ell}$	$\underline{m}$	$\underline{n}$	$\underline{p}$	Maximum displacement ($\text{\AA}$)
5 (1)	2-6	0.072	0.351	-0.934	1.416	0.04
5 (2)	19-23	0.028	0.228	-0.973	-1.733	0.08
6 (1)	7-12	0.598	0.626	-0.500	-0.333	0.16
6 (2)	13-18	0.736	-0.335	-0.588	1.348	0.10

Angles between planes

Planes	Angle
5 (1)-5 (2)	8°
5 (1)-6 (1)	43
5 (1)-6 (2)	61
6 (1)-6 (2)	58

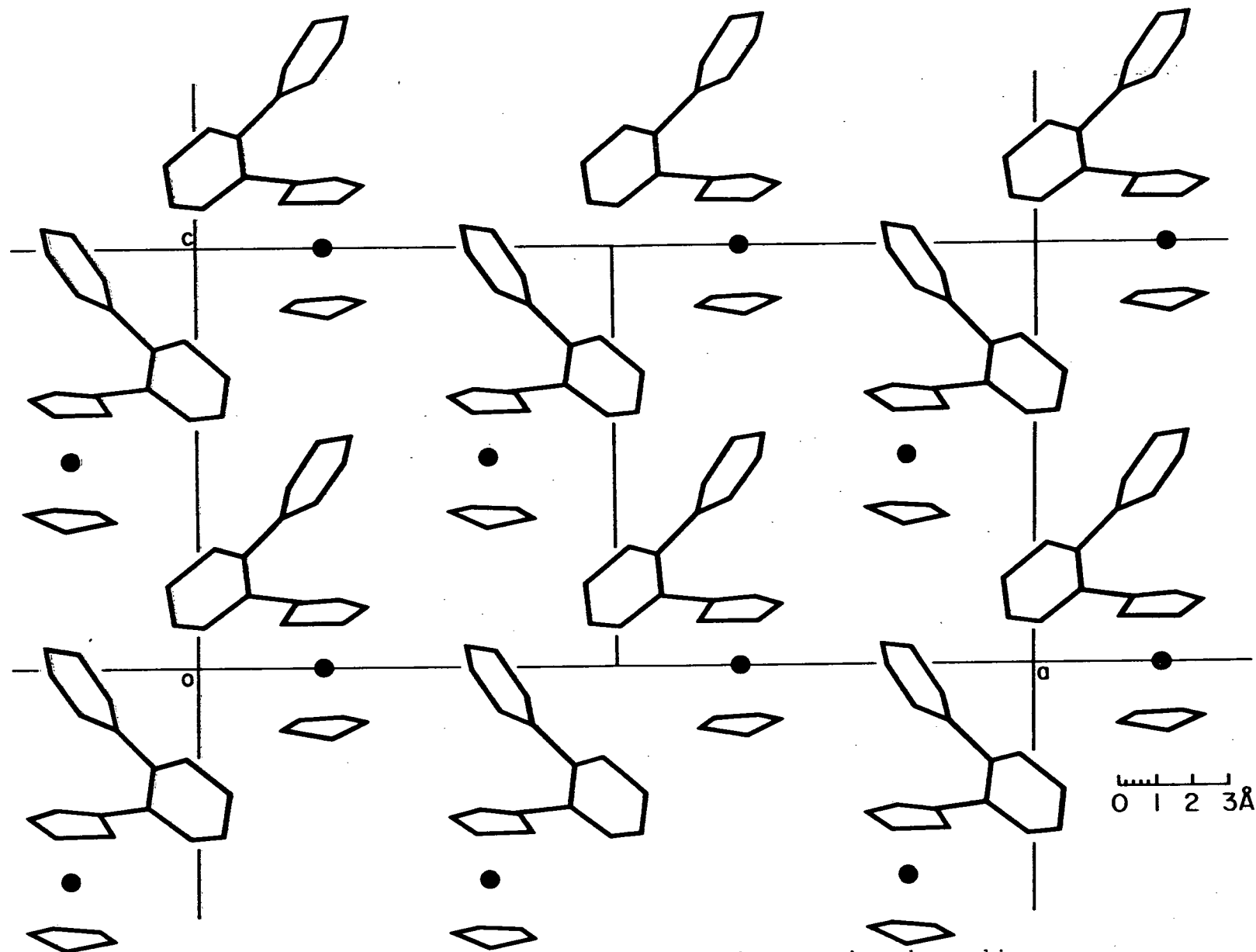


Figure 5. View of the structure along b , illustrating the packing of the molecules.

opposite directions and increase the C(6)...C(18) distance of about 1.5 Å in a planar model to 3.84 Å.

The relation between the cyclopentadienyl rings can be seen in Figure 6, which shows a view along the normal to their planes. The rings are approximately eclipsed, the average angle of rotation from the eclipsed position (calculation in Appendix I:B) being about 0°.

The mean bond distances and valency angles are, within the limits of experimental error, similar to those in related compounds.

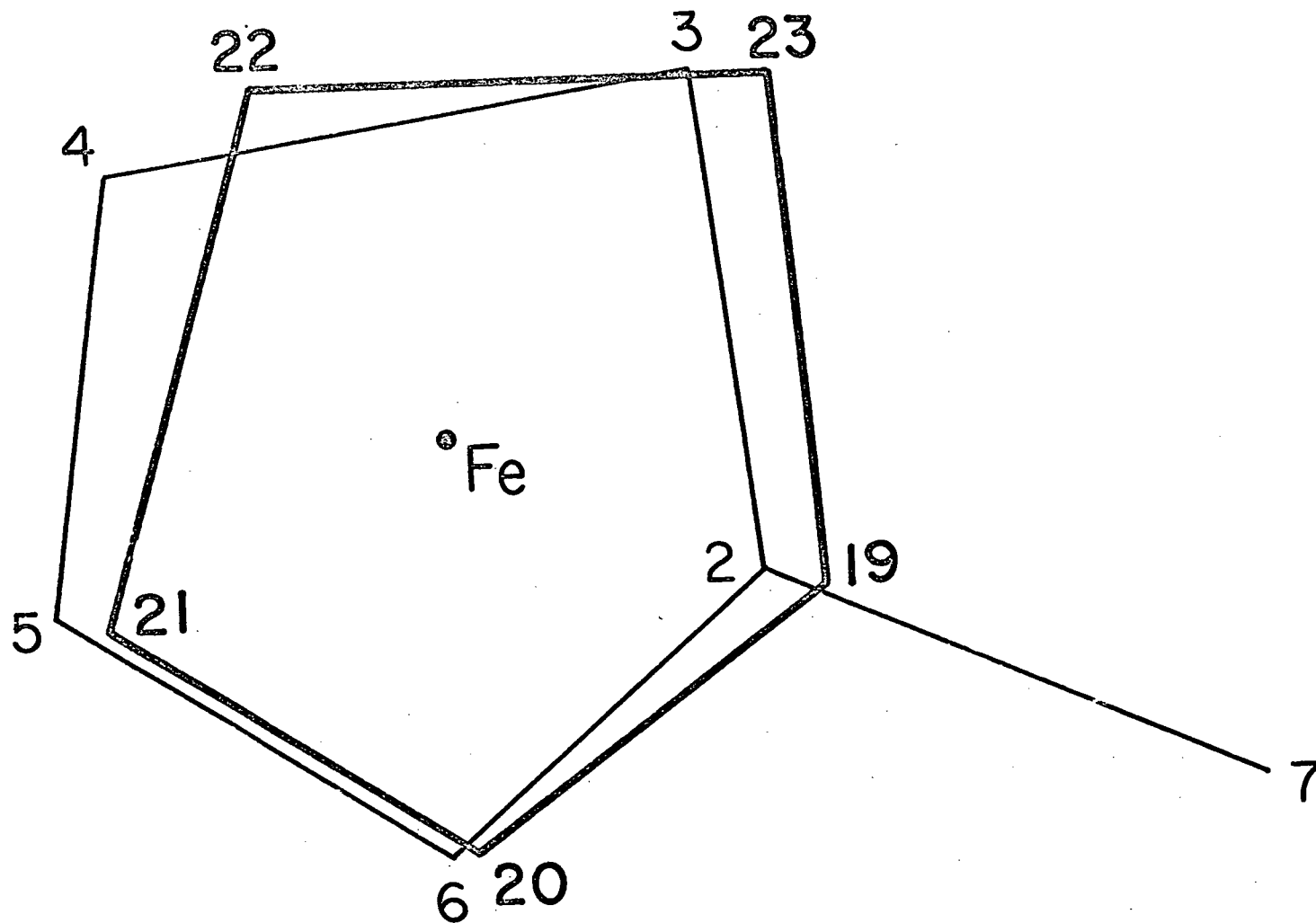


Figure 6. View of the cyclopentadienyl rings normal to their planes.
Heavier lines are nearer the viewer.

C. THE STRUCTURE OF 4-BIPHENYLYLFERROCENE

Experimental

Crystals of 4-biphenylylferrocene (28) are orange-yellow plates elongated along b . The density was measured by flotation in aqueous potassium iodide and the unit cell parameters and space group were determined from rotation and Weissenberg photographs and on a G.E. Spectrogoniometer.

Crystal data (λ , Cu- K_{α} = 1.5418 Å; λ , Fe- K_{α} = 1.9373 Å). 4-Biphenylylferrocene, $C_{22}H_{18}Fe$; M.W. = 338.2; m.p. = 164-165°.

Monoclinic, a = 19.18, b = 7.79, c = 10.85 Å, β = 91.8°.

U = 1620 Å³, D_m = 1.38, Z = 4, D_x = 1.39 g.cm.⁻³.

$F(000)$ = 704.

Absorption coefficients for X-rays, $\mu(Cu-K_{\alpha})$ = 76 cm.⁻¹, $\mu(Fe-K_{\alpha})$ = 25 cm.⁻¹.

Absent reflexions: $0k0$ when k is odd. Space group is $P2_1$ (C_2^2) or $P2_1/m$ (C_{2h}^2). $P2_1$ from structure analysis.

The intensities were measured on a General Electric XRD 5 Spectrogoniometer with Single Crystal Orienter, using a scintillation counter, approximately monochromatic Fe- K_{α} radiation (manganese filter and pulse height analyser), and a θ - 2θ scan. All reflexions with $2\theta(Fe-K_{\alpha}) \leq 148^\circ$ (minimum d = 1.0 Å) were examined and 1579 (87%) had measurable intensities. The intensities were corrected for background, which was approximately a function of θ only. The crystal used was mounted with b parallel to the ϕ axis of the goniostat and had cross-section 0.4 x 0.01 mm. Crystals of more uniform cross-section were not obtainable so that it was necessary to consider possible absorption errors. Because of the extreme thinness of the

crystal plate, absorption is serious only for planes in a few very narrow regions of reciprocal space (2), the maximum possible error in structure factor being about 30%. Since only a few planes have errors as large as this and because of the difficulty of making accurate estimations of the absorption, no corrections were applied. The possible errors could have been reduced to about half by using molybdenum radiation, but only at the expense of weaker, and hence, less reliable intensities. Lorentz and polarization factors were applied and the structure amplitudes were derived.

Structure Analysis

The Fe-Fe vectors in the three-dimensional Patterson function could be interpreted in terms of space group $A2/m$ with one independent iron atom situated on the mirror plane. A three-dimensional electron-density distribution computed with phases based on this arrangement had, of course, the corresponding symmetry, but the positions of possible carbon atom peaks indicated clearly that some of the symmetry elements were spurious (alternatively it would have been possible to retain mirror symmetry by allowing a disordered arrangement of molecules, but neither at this nor any other stage of the analysis was there any evidence to suggest disorder). The ambiguities were resolved by using chemical knowledge and by defining the positive direction of the y -axis by arbitrarily choosing one of the two possible molecular arrangements around one iron atom. There were then four possible arrangements around the second iron atom. Two of these could immediately be discarded since they corresponded to $A2$ and $P2_1/c$ symmetries. The other two each had space group $P2_1$ with two molecules in the asymmetric unit. Structure factors were calculated for both of these latter arrangements using scattering factors of the International Tables for X-ray

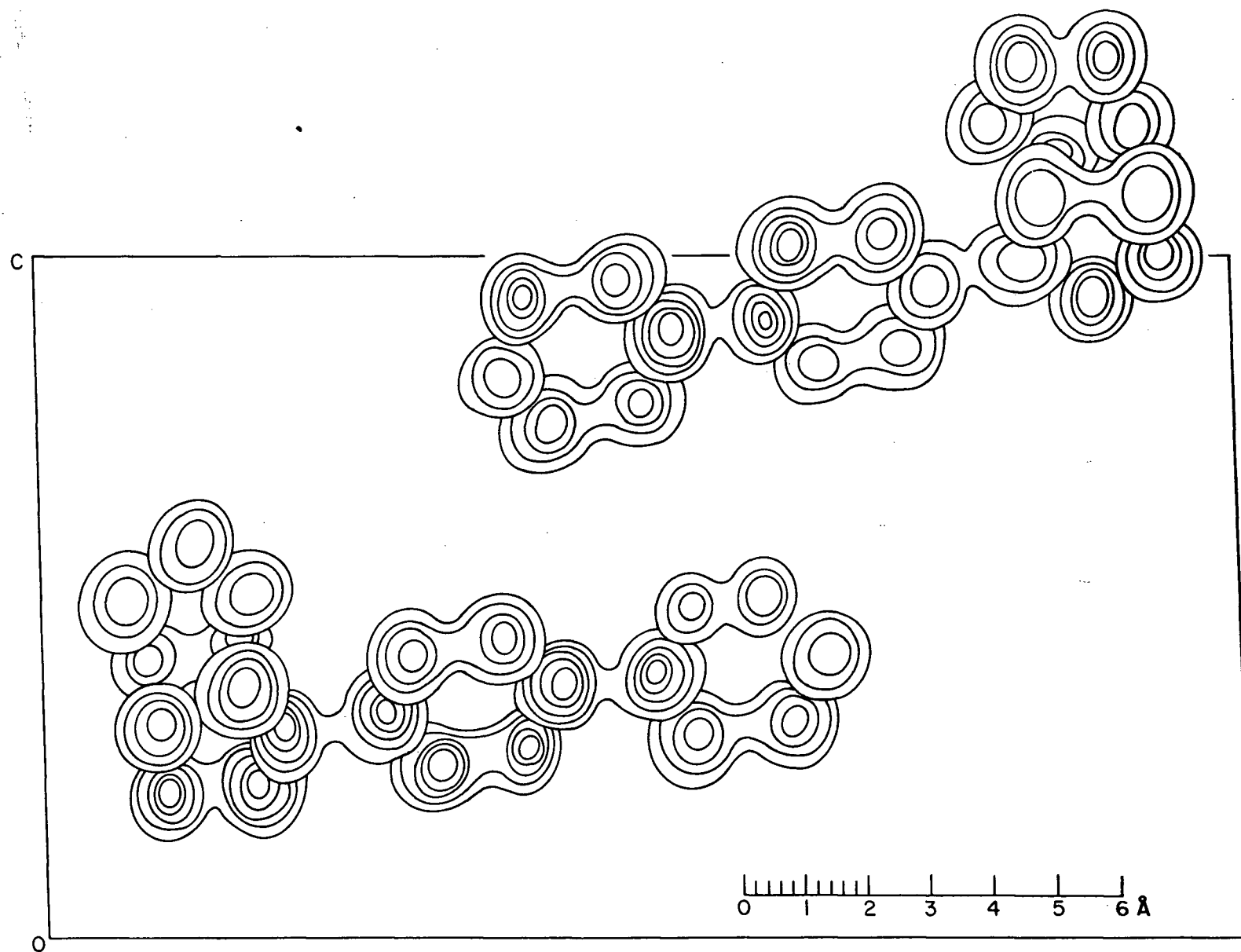


Figure 7. Superimposed sections of the three-dimensional electron-density distribution, through the atomic centres parallel to $(010)_3$. Contours are at intervals of $1 \text{ e. \AA}^{-3}$, starting at $2 \text{ e. \AA}^{-3}$.

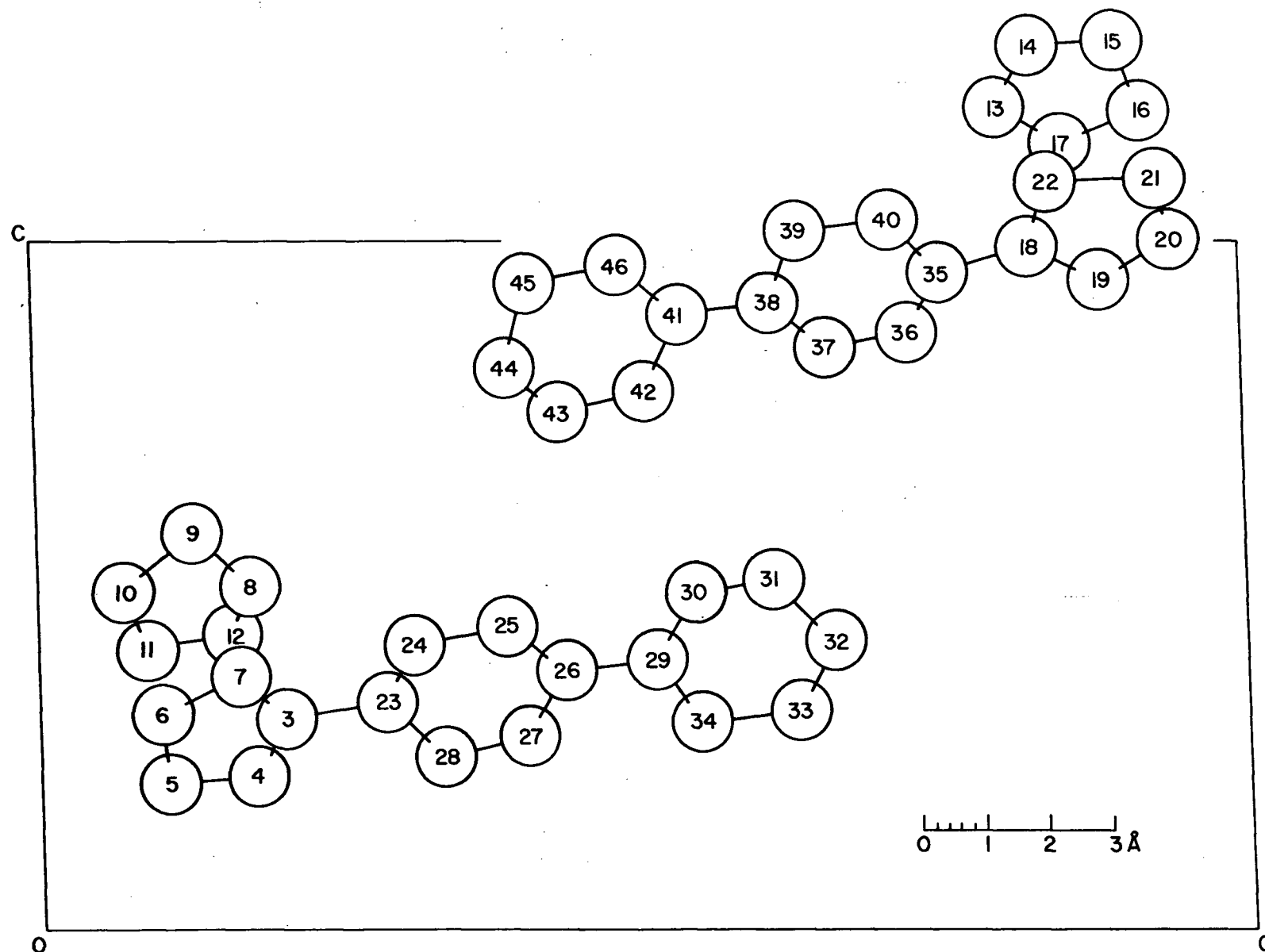


Figure 8. View of the structure giving the atom numbering used. In both Figure 7 and Figure 8 only the molecules with iron atoms at $y = 0$ are shown and the iron atoms, which are sandwiched between the five-membered rings, are omitted for clarity.

Crystallography (11) with $B = 4.0 \text{ \AA}^2$ for all atoms; the R factors were 0.38 and 0.43 for the two arrangements. Three cycles of least-squares refinement reduced these values to 0.20 and 0.31, so that the first arrangement seemed correct.

A three-dimensional electron-density map confirmed the derived structure and further refinement proceeded by block-diagonal least-squares methods, minimizing $\sum w(|F_o| - |F_c|)^2$, with $\sqrt{w} = |F_o|/20$ when $|F_o| < 20$ and $\sqrt{w} = 1$ when $|F_o| \geq 20$. Refinement was continued, initially with isotropic and finally with anisotropic thermal parameters, until the shifts were small and in random directions, the final R being 0.15 for the observed reflexions. Final measured and calculated structure factors are listed in Table IX. (Appendix II).

A final three-dimensional Fourier series was summed and superimposed sections of the resulting electron-density distribution are shown in Figure 7. Figure 8 is a drawing of the structure giving the atom numbering used for convenience in the analysis. A final difference map showed no significant spurious detail, the maximum fluctuations being $\pm 0.7 \text{ e. \AA}^{-3}$.

Coordinates and Molecular Dimensions

The final positional parameters are given in Table V. As a result of the possible absorption errors the individual values of the anisotropic thermal parameters probably have no real physical significance, and Table V includes only the final isotropic values.

The individual bond distances and angles are also not very accurate ($\sigma \sim 0.04 \text{ \AA}$ and 3°) and the average values only are given in Table VI. Table VI also gives the equations of the mean planes of the various rings; these were computed with inclusion of the atoms listed in the Table to

Table V.

Final positional (fractional $\times 10^3$) and isotropic thermal ($\text{\AA}^2$) parameters. Mean standard deviations are $\sigma(\underline{x}) = \sigma(\underline{y}) = \sigma(\underline{z}) = 0.004 \text{ \AA}$ for Fe, $0.03 \text{ \AA}$ for C; $\sigma(\underline{B}) = 0.1 \text{ \AA}^2$ for Fe, $0.8 \text{ \AA}^2$ for C.

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\underline{B}$
Fe(1)	135.4	0	385.5	5.4
2	126.7	-486.5	-119.2	5.7
C(3)	208	150	305	4.5
4	168	060	211	5.8
5	091	086	212	5.4
6	086	-220	308	3.6
7	158	248	356	4.7
8	194	-108	524	6.2
9	128	-038	577	5.9
10	069	-129	496	4.9
11	091	-241	422	7.5
12	173	-251	419	7.1
13	197	-651	-199	6.2
14	167	-540	-288	4.2
15	096	-573	-285	5.2
16	072	-689	-197	6.0
17	138	-754	-125	7.1
18	180	-333	008	4.6
19	125	-424	062	6.5
20	055	-396	017	3.4
21	069	-260	-082	6.8
22	147	-237	-086	5.2
23	283	149	325	4.6
24	312	247	420	5.0
25	386	245	445	6.1
26	432	135	356	4.9
27	395	046	262	4.4
28	325	053	241	5.6
29	506	138	377	3.3
30	537	212	484	3.7
31	610	209	499	5.8
32	657	133	414	7.3
33	622	061	307	4.4
34	549	055	282	5.6
35	260	-346	037	4.3
36	281	-459	133	4.7
37	352	-474	160	6.8
38	403	-370	088	5.3
39	377	-253	-010	4.5
40	306	-249	-034	4.9
41	480	-373	120	4.2
42	501	-462	228	4.4
43	573	-456	257	5.7
44	622	-384	184	6.5
45	599	-295	076	5.2
46	523	-297	043	4.6

Table VI.

Mean bond distances ($\sigma \sim 0.04 \text{ \AA}$) and valency angles ($\sigma \sim 3^\circ$),
equations of mean planes and angles between planes.

Distances and angles

Fe-C	2.07 $\text{\AA}$		
C-C (5-rings)	1.48	C-C-C (5-rings)	108°
C-C (6-rings)	1.43	C-C-C (6-rings)	120
C-C (between rings)	1.48		

Equations of mean planes, in the form $\underline{l}X' + \underline{m}Y + \underline{n}Z' + p = 0$, where
 X' , Y , Z' are coordinates in $\text{\AA}$ referred to orthogonal axes $\underline{a}, \underline{b}, \underline{c}^*$.

Plane	Atoms	$\underline{l}$	$\underline{m}$	$\underline{n}$	p	Maximum Displacement ($\text{\AA}$)
5(1)	3-7	0.135	0.725	-0.675	0.860	0.04
5(2)	8-12	0.032	0.718	-0.696	4.502	0.03
5(3)	18-22	0.106	-0.742	-0.662	-2.302	0.03
5(4)	13-17	0.094	-0.744	-0.662	-5.577	0.03
6(1)	23-28	0.100	0.790	-0.604	0.716	0.03
6(2)	29-34	0.070	0.875	-0.479	0.408	0.01
6(3)	35-40	0.095	-0.748	-0.657	-2.279	0.03
6(4)	41-46	0.113	-0.851	-0.513	-2.891	0.02

Angles between planes

Planes	Angle	Planes	Angle
5(1)-5(2)	6°	5(3)-5(4)	0°
5(1)-6(1)	6	5(3)-6(3)	0
5(1)-6(2)	15	5(3)-6(4)	11
6(1)-6(2)	9	6(3)-6(4)	10

define the rings and the atoms bonded directly to each ring. The maximum displacements from the planes are also given. All the intermolecular contacts correspond to van der Waals' interactions, the shortest C...C distances being 3.44 Å.

Discussion

The crystal structure analysis of 4-biphenylferrocene has shown that the unit cell contains two crystallographically independent molecules. All four rings in each molecule are approximately parallel, but with small twists which appear to be significant. In molecule 1 (containing Fe (1) and five-membered rings C(3)-C(7) and C(8)-C(12)) the angle between the two cyclopentadienyl rings is about 6°, the first six-membered ring of the biphenyl group is rotated about the C-C bond 6° out of the plane of the cyclopentadienyl ring to which it is bonded and the outer benzene ring is rotated by a further 9°. In molecule 2 the corresponding angles are 0°, 0° and 10°. The general arrangement in each molecule is therefore rather similar; the cyclopentadienyl rings are approximately parallel, the -C₆H₄- ring is perhaps slightly rotated from the five-membered ring plane and the -C₆H₅ ring exhibits a somewhat larger, but still relatively small displacement. So the biphenyl group in this molecule compares with the planar arrangement of biphenyl in the solid state (17), although there is a slight rotation of one ring plane with respect to the other. In 2-biphenylferrocene the angle of 58° between the planes of the two benzene rings can be compared with the 45° angle in biphenyl vapour (16). Thus, by their ring rotations the strain resulting from the close contact of the ortho hydrogens in completely planar biphenyl is relieved in both 4- and 2-biphenylferrocene, especially in the latter compound.

One of the principal objects of the investigation was the

determination of the arrangements of the cyclopentadienyl rings, which is illustrated in Figure 8 and more clearly in Figure 9, which shows views approximately along the normals to the ring planes. If the orientations are described in terms of the rotation of one of the rings from the fully eclipsed position, then molecule 1, with a rotation of about 15° (calculation in Appendix I:B), is approximately midway between the fully eclipsed (0°) and fully staggered (36°) arrangements and molecule 2, rotation about 5° , is nearly eclipsed (Figure 9). The observation of these two different arrangements in the same crystal supports the view that the orientations must be strongly dependent on intermolecular forces (26).

Also the displacements from coplanarity in the biphenyl groups in 4-biphenylferrocene and in 2-biphenylferrocene are further indication that there is no conjugation between the two phenyl rings, but probably it is the interactions between molecules which determine the biphenyl configuration.

The mean bond distances and valency angles are, within the limits of experimental error, similar to those in related molecules.

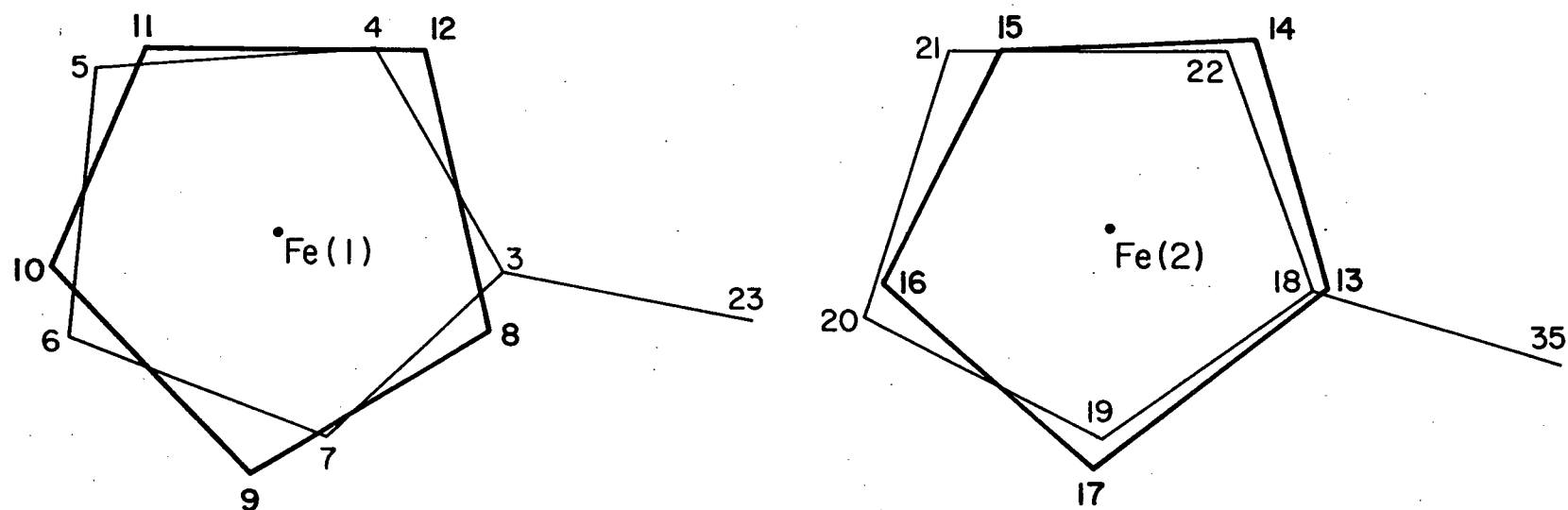


Figure 9. Views of the cyclopentadienyl rings normal to their planes.
Heavier lines are nearer the viewer.

APPENDIX I

DESCRIPTION OF SOME COMPUTER PROGRAMS WRITTEN
FOR SPECIAL CALCULATIONS IN THESE ANALYSES

A. ABSORPTION CORRECTION FOR THIN FLAT CRYSTALS

In the crystal structure analysis of β -dimethyltellurium diiodide all the reflexions were corrected for absorption according to the method of Zalkin, Forrester and Templeton (10) for thin, flat crystals.

The approximation is made that the absorption correction depends on the harmonic mean value $\underline{m}$ of $|\cos \underline{P}|$ and $|\cos \underline{Q}|$, where $\underline{P}$ and $\underline{Q}$ are the angles between the incident and diffracted beams, respectively, and the normal to the flat plate. Thus,

$$\frac{2}{\underline{m}} = \frac{1}{|\cos \underline{P}|} + \frac{1}{|\cos \underline{Q}|} \quad (1)$$

and $\underline{m}$ is inversely proportional to the path length of a beam scattered at the centre of the crystal.

By spherical trigonometry

$$|\cos \underline{P}| = |\cos \theta \cos \phi + \sin \theta \sin \phi \cos \chi| \quad (2)$$

$$|\cos \underline{Q}| = |\cos \theta \cos \phi - \sin \theta \sin \phi \cos \chi| \quad (3)$$

if the crystal is perpendicular to the incident beam when $\theta = \phi = 0$. θ , ϕ and χ are respectively, the Bragg angle, polar angle and inclination angle settings for the goniostat.

The equation used for the correction was

$$I(\text{corrected}) = \frac{I(\text{measured})}{1 + \underline{a} \exp(-\frac{\underline{b}}{\underline{m}})} \quad (4)$$

The intensities of the reflexions from the 002 and 006 planes which have $\chi = 90^\circ$ (and thus $\underline{m} = |\cos \underline{P}| = |\cos \underline{Q}| = |\cos \theta \cos \phi|$) were measured for $\phi = 0^\circ$ to 360° at intervals of 10° . The constants $\underline{a}$ and $\underline{b}$ were then determined from the graph of

$$\ln \left(\frac{I(\text{measured})}{I(\text{minimum})} - 1 \right) \quad \text{versus} \quad \left(\frac{1}{\cos \theta \cos \phi} \right)$$

This method; then, reduces the intensities of all reflexions with less than maximum absorption.

The following computer program calculates the absorption correction for each reflexion according to equation (4). The input required includes a and b, the constants obtained from the graph and ϕ_0 , the value of ϕ when $I(\text{measured})$ is maximum (i.e. when the crystal is perpendicular to the incident beam). The program also must read in the goniostat settings θ , χ and ϕ for each plane. The value of ϕ used in equation (4) is $\phi = \phi(\text{input}) - \phi_0$ so that $\phi = 0$ when $I(\text{measured})$ is maximum.

```

$FORTRAN
C      ABSORPTION CORRECTION - THIN FLAT CRYSTALS
      READ (5,1) A,B,PHIA
1      FORMAT(3F10.5)
3      READ (5,8) LFH,LFK,LFL,INT,SC,TWOTH,CHI,PHI
8      FORMAT(10X,3I3,2X,I5,3X,F6.2,11X,F8.3,2(1X,F8.3))
      TH=TWOTH/(2.*57.29578)
      PHE=(PHI+(360.-PHIA))/57.29578
22     CTCF=COS(TH)*COS(PHE)
      STSPC=SIN(TH)*SIN(PHE)*COS(CHI/57.29578)
      CSP=ABS(CTCF+STSPC)
      CSQ=ABS(CTCF-STSPC)
      CM=2.*CSP*CSQ/(CSQ+CSP)
      SCA=1./(1.+A*EXP(-B/CM))
      SC=SC*SCA*10.
      WRITE (6,8) LFH,LFK,LFL,INT,SC,TWOTH,CHI,PHI
      WRITE (7,8) LFH,LFK,LFL,INT,SC,TWOTH,CHI,PHI
      GO TO 3
      END
$ENTRY

```

B. ANGLE OF ROTATION FROM ECLIPSED POSITION

The following program was written to calculate the angle of rotation of the cyclopentadienyl rings from the fully eclipsed position in 2-biphenylferrocene and in 4-biphenylferrocene.

This involves projecting the two rings of a ferrocene group onto one plane, the direction cosines of which are the average of those of the ring planes, the rings being approximately parallel.

The equation of the average plane is

$$\lambda x + \mu y + \nu z + d = 0. \quad (1)$$

A set of orthogonal axes is calculated so that two axes are in the plane and one is perpendicular to it. Their direction cosines $(\lambda_1, \mu_1, \nu_1)$ are as follows:

$$(\lambda_3, \mu_3, \nu_3) = (\lambda, \mu, \nu) \quad (2)$$

$$(\lambda_1, \mu_1, \nu_1) = \left(\frac{x_1 - x_2}{r_1}, \frac{y_1 - y_2}{r_1}, \frac{z_1 - z_2}{r_1} \right) \quad (3)$$

where x_i, y_i, z_i are coordinates, with respect to the orthogonal axes a, b and c^{*}, of a point on the plane,

$$r_1 = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}.$$

$$(\lambda_2, \mu_2, \nu_2) = \left(\frac{\mu_1 \nu_3 - \mu_3 \nu_1}{r_2}, \frac{\nu_1 \lambda_3 - \nu_3 \lambda_1}{r_2}, \frac{\lambda_1 \mu_3 - \lambda_3 \mu_1}{r_2} \right) \quad (4)$$

$$\text{where } r_2 = \sqrt{(\mu_1 \nu_3 - \mu_3 \nu_1)^2 + (\nu_1 \lambda_3 - \nu_3 \lambda_1)^2 + (\lambda_1 \mu_3 - \lambda_3 \mu_1)^2}.$$

Each ring atom is projected onto the average plane by finding its new coordinates $(y_1, y_2, 0)$ with respect to the above orthogonal axes from its original coordinates (x_1, x_2, x_3) with respect to the orthogonal axes a, b and c^{*}.

$$(y_1, y_2, y_3) = (x_1, x_2, x_3) \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ \mu_1 & \mu_2 & \mu_3 \\ \nu_1 & \nu_2 & \nu_3 \end{pmatrix} \quad (5)$$

If the angle of rotation of one ring with respect to the other is defined as the angle θ between the projected Fe-C bond to a carbon atom on one ring and the projected Fe-C bond to the corresponding carbon on the other ring, then it is calculated as follows:

$$\cos \theta = \frac{(y_1(\text{Fe}) - y_1(\text{C}_1))(y_1(\text{Fe}) - y_1(\text{C}_2)) + (y_2(\text{Fe}) - y_2(\text{C}_1))(y_2(\text{Fe}) - y_2(\text{C}_2))}{\sqrt{[(y_1(\text{Fe}) - y_1(\text{C}_1))^2 + (y_2(\text{Fe}) - y_2(\text{C}_1))^2][(y_1(\text{Fe}) - y_1(\text{C}_2))^2 + (y_2(\text{Fe}) - y_2(\text{C}_2))^2]}} \quad (6)$$

where C_1 is a carbon atom in ring 1,

C_2 is the corresponding carbon atom in ring 2.

\$FORTRAN

```

C      ROTATION FROM ECLIPSED
      DIMENSION X1(11),X2(11),X3(11),Y1(11),Y2(11),Y3(11),A1(11),B1(11)
      DIMENSION R1(11)
      DO 25 I=1,11
      READ (5,8) X1(I),X2(I),X3(I)
8      FORMAT(4F8.5)
25     CONTINUE
      READ (5,8) WL,WU,WV,D
      WL3=WL
      WU3=WU
      WV3=WV
      X32=-(D+WL*X1(2)+WU*X2(2))/WV
      X35=-(D+WL*X1(5)+WU*X2(5))/WV
      AX=X1(2)-X1(5)
      BX=X2(2)-X2(5)
      C1=X32-X35
      RX=SQRT(AX*AX+BX*BX+C1*C1)
      WL1=AX/RX
      WU1=BX/RX
      WV1=C1/RX
      A2=WU1*WV3-WU3*WV1
      B2=WV1*WL3-WV3*WL1
      C2=WL1*WU3-WL3*WU1
      R2=SQRT(A2*A2+B2*B2+C2*C2)
      WL2=A2/R2
      WU2=B2/R2
      WV2=C2/R2
      DO 28 I=1,11
      Y1(I)=X1(I)*WL1+X2(I)*WU1+X3(I)*WV1
      Y2(I)=X1(I)*WL2+X2(I)*WU2+X3(I)*WV2
      WRITE (6,8) Y1(I),Y2(I)
28     CONTINUE
      DO 30 I=2,6
      A1(I)=Y1(1)-Y1(I)
      B1(I)=Y2(1)-Y2(I)
      R1(I)=SQRT(A1(I)*A1(I)+B1(I)*B1(I))
30     CONTINUE
      DO 35 J=7,11
      A1(J)=Y1(1)-Y1(J)
      B1(J)=Y2(1)-Y2(J)
      R1(J)=SQRT(A1(J)*A1(J)+B1(J)*B1(J))
35     CONTINUE
      DO 38 I=2,6
      J=I+5
      C=(A1(I)*A1(J)+B1(I)*B1(J))/(R1(I)*R1(J))
      ANG=57.296*ATAN(SQRT((1.0-C*C)/(C*C)))
      WRITE (6,9) I,J,ANG
9      FORMAT(2I4,F10.5)
38     CONTINUE
      END
$ENTRY

```

APPENDIX II

TABLES OF OBSERVED AND CALCULATED STRUCTURE FACTORS

Table VII.

8-Dimethyltellurium diiodide measured

and calculated structure factors

h	k	l	F _o	F _c
0	0	0	127.4	127.4
0	0	1	114.3	114.3
0	0	2	100.8	100.8
0	0	3	87.4	87.4
0	0	4	74.0	74.0
0	0	5	60.6	60.6
0	0	6	47.2	47.2
0	0	7	33.8	33.8
0	0	8	20.4	20.4
0	0	9	7.0	7.0
0	1	0	114.3	114.3
0	1	1	100.8	100.8
0	1	2	87.4	87.4
0	1	3	74.0	74.0
0	1	4	60.6	60.6
0	1	5	47.2	47.2
0	1	6	33.8	33.8
0	1	7	20.4	20.4
0	1	8	7.0	7.0
0	1	9	114.3	114.3
0	2	0	100.8	100.8
0	2	1	87.4	87.4
0	2	2	74.0	74.0
0	2	3	60.6	60.6
0	2	4	47.2	47.2
0	2	5	33.8	33.8
0	2	6	20.4	20.4
0	2	7	7.0	7.0
0	2	8	100.8	100.8
0	2	9	87.4	87.4
0	3	0	87.4	87.4
0	3	1	74.0	74.0
0	3	2	60.6	60.6
0	3	3	47.2	47.2
0	3	4	33.8	33.8
0	3	5	20.4	20.4
0	3	6	7.0	7.0
0	3	7	87.4	87.4
0	3	8	74.0	74.0
0	3	9	60.6	60.6
0	4	0	74.0	74.0
0	4	1	60.6	60.6
0	4	2	47.2	47.2
0	4	3	33.8	33.8
0	4	4	20.4	20.4
0	4	5	7.0	7.0
0	4	6	74.0	74.0
0	4	7	60.6	60.6
0	4	8	47.2	47.2
0	4	9	33.8	33.8
0	5	0	60.6	60.6
0	5	1	47.2	47.2
0	5	2	33.8	33.8
0	5	3	20.4	20.4
0	5	4	7.0	7.0
0	5	5	60.6	60.6
0	5	6	47.2	47.2
0	5	7	33.8	33.8
0	5	8	20.4	20.4
0	5	9	7.0	7.0
0	6	0	47.2	47.2
0	6	1	33.8	33.8
0	6	2	20.4	20.4
0	6	3	7.0	7.0
0	6	4	47.2	47.2
0	6	5	33.8	33.8
0	6	6	20.4	20.4
0	6	7	7.0	7.0
0	6	8	47.2	47.2
0	6	9	33.8	33.8
0	7	0	33.8	33.8
0	7	1	20.4	20.4
0	7	2	7.0	7.0
0	7	3	33.8	33.8
0	7	4	20.4	20.4
0	7	5	7.0	7.0
0	7	6	33.8	33.8
0	7	7	20.4	20.4
0	7	8	7.0	7.0
0	7	9	33.8	33.8
0	8	0	20.4	20.4
0	8	1	7.0	7.0
0	8	2	33.8	33.8
0	8	3	20.4	20.4
0	8	4	7.0	7.0
0	8	5	33.8	33.8
0	8	6	20.4	20.4
0	8	7	7.0	7.0
0	8	8	33.8	33.8
0	8	9	20.4	20.4
0	9	0	7.0	7.0
0	9	1	33.8	33.8
0	9	2	20.4	20.4
0	9	3	7.0	7.0
0	9	4	33.8	33.8
0	9	5	20.4	20.4
0	9	6	7.0	7.0
0	9	7	33.8	33.8
0	9	8	20.4	20.4
0	9	9	7.0	7.0
1	0	0	127.4	127.4
1	0	1	114.3	114.3
1	0	2	100.8	100.8
1	0	3	87.4	87.4
1	0	4	74.0	74.0
1	0	5	60.6	60.6
1	0	6	47.2	47.2
1	0	7	33.8	33.8
1	0	8	20.4	20.4
1	0	9	7.0	7.0
1	1	0	114.3	114.3
1	1	1	100.8	100.8
1	1	2	87.4	87.4
1	1	3	74.0	74.0
1	1	4	60.6	60.6
1	1	5	47.2	47.2
1	1	6	33.8	33.8
1	1	7	20.4	20.4
1	1	8	7.0	7.0
1	1	9	114.3	114.3
1	2	0	100.8	100.8
1	2	1	87.4	87.4
1	2	2	74.0	74.0
1	2	3	60.6	60.6
1	2	4	47.2	47.2
1	2	5	33.8	33.8
1	2	6	20.4	20.4
1	2	7	7.0	7.0
1	2	8	100.8	100.8
1	2	9	87.4	87.4
1	3	0	87.4	87.4
1	3	1	74.0	74.0
1	3	2	60.6	60.6
1	3	3	47.2	47.2
1	3	4	33.8	33.8
1	3	5	20.4	20.4
1	3	6	7.0	7.0
1	3	7	87.4	87.4
1	3	8	74.0	74.0
1	3	9	60.6	60.6
1	4	0	74.0	74.0
1	4	1	60.6	60.6
1	4	2	47.2	47.2
1	4	3	33.8	33.8
1	4	4	20.4	20.4
1	4	5	7.0	7.0
1	4	6	74.0	74.0
1	4	7	60.6	60.6
1	4	8	47.2	47.2
1	4	9	33.8	33.8
1	5	0	60.6	60.6
1	5	1	47.2	47.2
1	5	2	33.8	33.8
1	5	3	20.4	20.4
1	5	4	7.0	7.0
1	5	5	60.6	60.6
1	5	6	47.2	47.2
1	5	7	33.8	33.8
1	5	8	20.4	20.4
1	5	9	7.0	7.0
1	6	0	47.2	47.2
1	6	1	33.8	33.8
1	6	2	20.4	20.4
1	6	3	7.0	7.0
1	6	4	47.2	47.2
1	6	5	33.8	33.8
1	6	6	20.4	20.4
1	6	7	7.0	7.0
1	6	8	47.2	47.2
1	6	9	33.8	33.8
1	7	0	33.8	33.8
1	7	1	20.4	20.4
1	7	2	7.0	7.0
1	7	3	33.8	33.8
1	7	4	20.4	20.4
1	7	5	7.0	7.0
1	7	6	33.8	33.8
1	7	7	20.4	20.4
1	7	8	7.0	7.0
1	7	9	33.8	33.8
1	8	0	20.4	20.4
1	8	1	7.0	7.0
1	8	2	33.8	33.8
1	8	3	20.4	20.4
1	8	4	7.0	7.0
1	8	5	33.8	33.8
1	8	6	20.4	20.4
1	8	7	7.0	7.0
1	8	8	33.8	33.8
1	8	9	20.4	20.4
1	9	0	7.0	7.0
1	9	1	33.8	33.8
1	9	2	20.4	20.4
1	9	3	7.0	7.0
1	9	4	33.8	33.8
1	9	5	20.4	20.4
1	9	6	7.0	7.0
1	9	7	33.8	33.8
1	9	8	20.4	20.4
1	9	9	7.0	7.0
2	0	0	127.4	127.4
2	0	1	114.3	114.3
2	0	2	100.8	100.8
2	0	3	87.4	87.4
2	0	4	74.0	74.0
2	0	5	60.6	60.6
2	0	6	47.2	47.2
2	0	7	33.8	33.8
2	0	8	20.4	20.4
2	0	9	7.0	7.0
2	1	0	114.3	114.3
2	1	1	100.8	100.8
2	1	2	87.4	87.4
2	1	3	74.0	74.0
2	1	4	60.6	60.6
2	1	5	47.2	47.2
2	1	6	33.8	33.8
2	1	7	20.4	20.4
2	1	8	7.0	7.0
2	1	9	114.3	114.3
2	2	0	100.8	100.8
2	2	1	87.4	87.4
2	2	2	74.0	74.0
2	2	3	60.6	60.6
2	2	4	47.2	47.2
2	2	5	33.8	33.8
2	2	6	20.4	20.4
2	2	7	7.0	7.0
2	2	8	100.8	100.8
2	2	9	87.4	87.4
2	3	0	87.4	87.4
2	3	1	74.0	74.0
2	3	2	60.6	60.6
2	3	3	47.2	47.2
2	3	4	33.8	33.8
2	3	5	20.4	20.4
2	3	6	7.0	7.0
2	3	7	87.4	87.4
2	3	8	74.0	74.0
2	3	9	60.6	60.6
2	4	0	74.0	74.0
2	4	1	60.6	60.6
2	4	2	47.2	47.2
2	4	3	33.8	33.8
2	4	4	20.4	20.4
2	4	5	7.0	7.0
2	4	6	74.0	74.0
2	4	7	60.6	60.6
2	4	8	47.2	47.2
2	4	9	33.8	33.8
2	5	0	60.6	60.6
2	5	1	47.2	47.2
2	5	2	33.8	33.8
2	5	3	20.4	20.4
2	5	4	7.0	7.0
2	5	5	60.6	60.6
2	5	6	47.2	47.2
2	5	7	33.8	33.8
2	5	8	20.4	20.4
2	5	9	7.0	7.0
2	6	0	47.2	47.2
2	6	1	33.8	33.8
2	6	2	20.4	20.4
2	6	3	7.0	7.0
2	6	4	47.2	47.2
2	6	5	33.8	33.8
2	6	6	20.4	20.4
2	6	7	7.0	7.0
2	6	8	47.2	47.2
2	6	9	33.8	33.8
2	7	0	33.8	33.8
2	7	1	20.4	20.4
2	7	2	7.0	7.0
2	7	3	33.8	33.8
2	7	4	20.4	20.4
2	7	5	7.0	7.0
2	7	6	33.8	33.8
2	7	7	20.4	20.4
2	7	8	7.0	7.0
2	7	9	33.8	33.8
2	8	0	20.4	20.4
2	8	1	7.0	7.0
2	8	2	33.8	33.8
2	8	3	20.4	20.4
2	8	4	7.0	7.0
2	8	5	33.8	33.8
2	8	6	20.4	20.4
2	8	7	7.0	7.0
2	8	8	33.8	33.8
2	8	9	20.4	20.4
2	9	0	7.0	7.0
2	9	1	33.8	33.8
2	9	2	20.4	20.4
2	9	3	7.0	7.0
2	9	4	33.8	33.8
2	9	5	20.4	20.4
2	9	6	7.0	7.0
2	9	7	33.8	33.8
2	9			

Table VII.

CONTINUED:									
h	k	l	F ₀	F _c					
-3	3	5	106.0	108.0	-3	9	6	19.6	14.5
-3	3	6	33.1	-11.7	-3	9	7	32.6	-32.9
-3	3	7	48.8	-49.0	-3	9	8	23.6	-15.7
-3	3	8	46.3	-38.7	-3	10	0	48.0	-18.3
-3	3	9	28.0	16.0	-3	10	1	-13.0	-31.7
-3	4	0	143.9	-141.4	-3	10	2	32.5	-37.0
-3	4	1	304.8	-333.4	-3	10	3	135.1	146.9
-3	4	2	194.2	217.2	-3	10	4	96.0	-101.5
-3	4	3	129.0	127.4	-3	10	5	73.0	71.3
-3	4	4	101.6	-99.7	-3	10	6	118.4	129.7
-3	4	5	78.2	89.9	-3	10	7	69.2	-74.7
-3	4	6	148.2	146.0	-3	10	8	57.3	-32.8
-3	4	7	275.1	259.4	-3	10	9	118.6	-119.4
-3	4	8	94.1	-93.7	-3	10	10	116.2	108.1
-3	4	9	30.5	-29.9	-3	11	0	-11.9	-11.4
-3	5	0	67.6	56.7	-3	11	1	-12.5	-7.3
-3	5	1	121.1	-11.2	-3	11	2	-13.2	-5.3
-3	5	2	31.1	-36.3	-3	11	3	-14.4	8.2
-3	5	3	24.7	25.7	-3	11	4	100.7	107.1
-3	5	4	102.0	91.1	-3	11	5	68.5	-63.1
-3	5	5	164.5	171.1	-3	11	6	88.1	-98.3
-3	5	6	72.5	70.2	-3	11	7	170.8	-178.5
-3	5	7	101.4	107.9	-3	11	8	113.2	-117.8
-3	5	8	10.6	-14.9	-3	11	9	153.4	-145.2
-3	5	9	15.7	9.3	-3	12	0	101.6	-111.1
-3	6	0	81.7	-83.7	-3	12	1	-17.2	22.5
-3	6	1	144.1	-147.5	-3	12	2	-18.7	9.4
-3	6	2	63.3	-65.3	-3	12	3	-18.7	9.4
-3	6	3	35.2	38.5	-3	12	4	223.0	-245.2
-3	6	4	23.2	21.4	-3	12	5	-19.6	15.6
-3	6	5	69.6	-71.5	-3	12	6	36.5	-33.7
-3	6	6	92.9	91.7	-3	12	7	82.9	87.1
-3	6	7	29.3	-22.3	-3	12	8	116.9	-108.0
-3	6	8	9.7	8.7	-3	12	9	107.2	108.9
-3	6	9	28.6	-28.4	-3	13	0	-14.1	-6.5
-3	7	0	147.7	-149.6	-3	13	1	116.9	-108.0
-3	7	1	131.7	-131.0	-3	13	2	116.9	-108.0
-3	7	2	34.8	33.6	-3	13	3	161.3	-173.5
-3	7	3	12.7	-18.3	-3	13	4	103.7	-105.8
-3	7	4	30.5	-30.5	-3	13	5	120.7	-120.7
-3	7	5	97.9	-89.0	-3	13	6	169.6	-169.6
-3	7	6	88.6	76.2	-3	13	7	216.4	-216.4
-3	7	7	117.7	-117.7	-3	13	8	169.6	-169.6
-3	7	8	213.7	-219.2	-3	13	9	216.4	-216.4
-3	7	9	182.0	-196.1	-3	14	0	-14.1	-6.5
-3	8	0	105.5	104.5	-3	14	1	116.9	-108.0
-3	8	1	101.9	112.4	-3	14	2	169.6	-169.6
-3	8	2	194.7	203.3	-3	14	3	216.4	-216.4
-3	8	3	35.6	-62.6	-3	14	4	169.6	-169.6
-3	8	4	49.2	52.1	-3	14	5	216.4	-216.4
-3	8	5	151.3	-165.0	-3	14	6	169.6	-169.6
-3	8	6	9.7	8.4	-3	14	7	216.4	-216.4
-3	8	7	111.7	-112.5	-3	14	8	169.6	-169.6
-3	8	8	28.5	-24.2	-3	14	9	216.4	-216.4
-3	8	9	52.6	-52.6	-3	15	0	-14.1	-6.5
-3	9	0	115.5	135.3	-3	15	1	169.6	-169.6
-3	9	1	79.5	79.5	-3	15	2	216.4	-216.4
-3	9	2	25.2	-22.5	-3	15	3	169.6	-169.6
-3	9	3	10.6	-10.3	-3	15	4	216.4	-216.4
-3	9	4	214.5	275.3	-3	15	5	169.6	-169.6
-3	9	5	21.2	-21.2	-3	15	6	216.4	-216.4
-3	9	6	71.2	-69.9	-3	15	7	169.6	-169.6
-3	9	7	61.3	-61.3	-3	15	8	216.4	-216.4
-3	9	8	150.0	159.1	-3	15	9	169.6	-169.6
-3	9	9	42.8	-38.9	-3	16	0	-14.1	-6.5
-3	9	0	35.7	40.9	-3	16	1	169.6	-169.6
-3	9	1	128.1	-141.3	-3	16	2	216.4	-216.4
-3	9	2	70.2	-73.5	-3	16	3	169.6	-169.6
-3	9	3	23.5	-28.5	-3	16	4	216.4	-216.4
-3	9	4	32.3	-33.6	-3	16	5	169.6	-169.6
-3	9	5	14.4	18.1	-3	16	6	216.4	-216.4
-3	9	6	63.8	64.2	-3	16	7	169.6	-169.6
-3	9	7	12.0	12.1	-3	16	8	216.4	-216.4
-3	9	8	49.0	-54.2	-3	16	9	169.6	-169.6
-3	9	9	107.9	120.9	-3	17	0	-14.1	-6.5
-3	9	0	20.4	-20.4	-3	17	1	169.6	-169.6
-3	9	1	114.8	-119.5	-3	17	2	216.4	-216.4
-3	9	2	152.0	161.8	-3	17	3	169.6	-169.6
-3	9	3	12.5	-15.4	-3	17	4	216.4	-216.4
-3	9	4	39.6	-36.9	-3	17	5	169.6	-169.6
-3	9	5	171.7	-191.5	-3	17	6	216.4	-216.4
-3	9	6	26.2	-23.1	-3	17	7	169.6	-169.6
-3	9	7	13.9	5.3	-3	17	8	216.4	-216.4
-3	9	8	10.7	-5.8	-3	17	9	169.6	-169.6
-3	9	9	45.2	45.2	-3	17	0	-14.1	-6.5

Table VIII.

2-Biphenyllylferrocene measured and calculated
structure factors.

h	k	l	F _o	F _c
4	0	0	166.1	174.9
6	0	0	151.5	150.0
8	0	0	0.0	0.7
10	0	0	26.7	26.2
12	0	0	16.5	18.6
14	0	0	0.0	11.0
16	0	0	23.5	28.6
18	0	0	15.0	14.2
20	0	0	13.4	16.0
22	0	0	13.4	13.2
2	0	1	107.7	116.6
4	0	1	76.2	81.9
6	0	1	18.1	31.6
8	0	1	25.9	32.6
10	0	1	17.1	20.2
12	0	1	26.9	30.2
14	0	1	17.3	21.1
16	0	1	0.0	3.2
18	0	1	18.1	22.5
20	0	1	18.9	28.1
0	2	0	78.1	79.6
2	2	0	87.1	93.1
4	2	0	121.4	120.0
6	2	0	90.6	94.6
8	2	0	32.4	36.1
10	2	0	40.2	41.2
12	2	0	22.2	30.9
14	2	0	19.0	22.4
16	2	0	24.0	24.6
18	2	0	12.9	11.1
2	0	2	43.0	46.1
4	0	2	32.4	33.7
6	0	2	48.1	45.6
8	0	2	67.6	66.3
10	0	2	20.1	25.5
12	0	2	38.7	40.1
14	0	2	33.3	33.7
16	0	2	21.3	24.6
18	0	2	22.7	21.5
0	4	0	52.5	49.7
2	4	0	7.5	12.4
4	4	0	7.9	12.9
6	4	0	63.2	56.7
8	4	0	22.5	13.7
10	4	0	77.5	82.7
12	4	0	27.6	27.9
14	4	0	25.4	32.0
16	4	0	17.8	16.0
18	4	0	18.8	11.7
2	0	4	33.2	34.8
4	0	4	19.8	27.3
6	0	4	42.9	43.9
8	0	4	36.8	38.4
10	0	4	15.2	9.1
12	0	4	47.7	47.5
14	0	4	12.4	14.8
0	6	0	64.0	64.1
2	6	0	38.6	40.5
4	6	0	65.1	62.6
6	6	0	31.1	28.8
8	6	0	0.0	9.9
10	6	0	25.9	30.0
12	6	0	17.3	14.4
14	6	0	12.9	9.5
2	0	6	76.1	67.6
4	0	6	16.3	22.0
6	0	6	7.0	10.6
8	0	6	19.1	28.2
10	0	6	7.0	8.1
12	0	6	7.0	6.8
0	8	0	47.1	43.7
2	8	0	15.1	18.9
4	8	0	24.1	27.5
6	8	0	21.4	17.0
8	8	0	9.8	6.1
2	0	8	17.2	9.0
4	0	8	25.8	21.5
6	0	8	21.9	17.8
0	10	0	28.7	25.1
2	10	0	18.9	9.1
4	10	0	12.0	4.6
2	0	10	26.9	16.8
4	0	10	0.0	0.4
6	0	10	18.7	4.5
2	1	0	64.1	74.2
3	1	0	33.6	40.1
4	1	0	134.6	132.8
5	1	0	15.2	20.9
6	1	0	17.1	24.5
7	1	0	0.0	1.1
8	1	0	10.5	19.9
9	1	0	12.8	12.6
10	1	0	13.6	17.2
11	1	0	14.5	3.4
12	1	0	13.6	14.3
13	1	0	14.3	5.7
14	1	0	15.2	27.8
15	1	0	0.0	23.0
16	1	0	0.0	17.8
17	1	0	0.0	3.7
18	1	0	15.2	15.7
19	1	0	0.0	13.2
20	1	0	15.8	23.9
1	1	1	36.3	38.4
2	1	1	147.2	157.4
3	1	1	86.8	87.9
4	1	1	63.5	72.4
5	1	1	29.3	30.5
6	1	1	18.6	22.2
7	1	1	11.8	5.6
8	1	1	72.1	67.8
9	1	1	14.9	16.2
10	1	1	13.0	5.6
11	1	1	0.0	11.7
12	1	1	0.0	15.8
13	1	1	17.3	12.0
14	1	1	22.5	27.5
15	1	1	0.0	9.8
16	1	1	20.0	18.1
0	1	2	69.2	77.7
1	1	2	37.2	46.7
2	1	2	28.0	23.1
3	1	2	34.3	34.1
4	1	2	30.8	31.4
5	1	2	19.7	23.4
6	1	2	46.3	51.2
7	1	2	22.5	22.2
8	1	2	39.3	41.7
9	1	2	0.0	11.7
10	1	2	45.3	47.3
11	1	2	28.6	33.5
12	1	2	0.0	7.9
13	1	2	0.0	16.4
14	1	2	23.6	30.7
15	1	2	0.0	8.3
16	1	2	27.3	30.7
17	1	2	0.0	12.2
18	1	2	21.7	11.3
19	1	2	0.0	5.3
20	1	2	22.5	15.8
1	1	3	21.9	25.8
2	1	3	22.4	23.3
3	1	3	56.1	64.3
4	1	3	56.1	60.4
5	1	3	0.0	14.6
6	1	3	25.9	35.3
7	1	3	22.4	22.7
8	1	3	51.8	48.5
9	1	3	26.2	30.2
10	1	3	27.1	28.6
11	1	3	0.0	11.1
12	1	3	52.7	46.2
13	1	3	0.0	6.8
14	1	3	19.3	22.7
15	1	3	0.0	7.8
16	1	3	18.6	7.3
0	1	4	0.0	21.6
1	1	4	12.6	9.3
2	1	4	0.0	15.3
3	1	4	13.0	16.8
4	1	4	41.5	45.6
5	1	4	17.0	19.4
6	1	4	32.2	39.5
7	1	4	0.0	12.3
8	1	4	24.7	22.8
9	1	4	0.0	1.9
10	1	4	63.7	66.3
11	1	4	0.0	6.4
12	1	4	18.5	14.9
13	1	4	0.0	7.2
14	1	4	17.9	27.0
1	1	5	13.7	18.5
2	1	5	54.5	54.5
3	1	5	8.1	9.1
4	1	5	21.4	24.4
5	1	5	15.5	21.0
6	1	5	0.0	12.9
7	1	5	14.7	24.4
8	1	5	62.5	54.7
9	1	5	0.0	7.9
10	1	5	14.1	15.8
11	1	5	0.0	13.3
12	1	5	17.5	20.3
13	1	5	0.0	9.3
14	1	5	18.7	22.6
0	1	6	79.2	75.8
1	1	6	39.2	34.1
2	1	6	11.6	17.3
3	1	6	0.0	10.7
4	1	6	50.6	44.7
5	1	6	17.2	16.7
6	1	6	39.3	34.1
7	1	6	0.0	6.9
8	1	6	0.0	2.0
9	1	6	0.0	9.9
10	1	6	34.0	31.4
1	1	7	0.0	6.3
2	1	7	60.8	58.7
3	1	7	18.4	22.0
4	1	7	34.9	32.6
5	1	7	18.9	10.5
6	1	7	27.3	28.0
7	1	7	0.0	9.0
8	1	7	19.0	31.3
9	1	7	14.5	8.1
0	1	8	28.2	23.5
1	1	8	19.0	12.4
2	1	8	20.1	12.8
3	1	8	15.2	2.1
4	1	8	10.9	9.5
5	1	8	16.3	22.5
6	1	8	22.5	13.7
7	1	8	38.2	43.1
8	1	8	14.8	16.7
9	1	8	63.4	62.2
0	1	9	0.0	3.0
1	1	9	30.8	28.7
2	1	9	19.7	16.0
3	1	9	40.6	39.0
4	1	9	15.4	13.2
5	1	9	9.4	1.9
6	1	9	0.0	2.4
7	1	9	14.7	22.5
8	1	9	0.0	8.4
9	1	9	19.6	21.2
0	1	10	17.3	21.7
1	1	10	33.7	35.5
2	1	10	38.2	33.0
3	1	10	46.8	41.3
4	1	10	0.0	18.0
5	1	10	29.8	28.5
6	1	10	19.5	32.6
7	1	10	30.7	28.5
8	1	10	14.6	22.7
9	1	10	0.0	11.9
10	1	10	12.7	20.5
11	1	10	22.4	25.7
12	1	10	12.6	18.3
13	1	10	21.0	13.8
14	1	10	0.0	6.0
15	1	10	14.4	10.1
16	1	10	16.6	25.0
17	1	10	15.2	28.3
18	1	10	47.7	43.2
19	1	10	0.0	6.5
20	1	10	33.1	33.3
1	1	11	28.7	28.6
2	1	11	57.4	57.5
3	1	11	49.6	49.6
4	1	11	30.6	29.6
5	1	11	22.4	24.5
6	1	11	0.0	3.9
7	1	11	19.5	20.7
8	1	11	52.5	49.6
9	1	11	20.6	29.1
10	1	11	9.7	13.7
11	1	11	0.0	15.2
12	1	11	18.5	24.9
13	1	11	31.3	31.3
14	1	11	32.7	30.4
15	1	11	16.1	17.0
16	1	11	17.3	25.0
17	1	11	16.0	10.2
18	1	11	0.0	10.3
19	1	11	9.4	15.6
20	1	11	74.2	64.2
1	1	12	0.0	19.2
2	1	12	9.2	3.3
3	1	12	0.0	14.4
4	1	12	35.0	33.5
5	1	12	0.0	12.2
6	1	12	11.0	23.9
7	1	12	0.0	1.7
8	1	12	11.7	17.0
9	1	12	72.4	69.6
10	1	12	15.7	26.2
11	1	12	0.0	8.9
12	1	12	16.2	20.8
13	1	12	29.1	35.5
14	1	12	5.1	8.7
15	1	12	58.6	48.4
16	1	12	23.0	25.3
17	1	12	0.0	10.5
18	1	12	26.6	25.0
19	1	12	26.0	22.2
20	1	12	0.0	15.1
1	1	13	21.2	27.7
2	1	13	0.0	4.6
3	1	13	16.1	12.2
4	1	13	0.0	7.9
5	1	13	57.7	54.5
6	1	13	29.7	24.0
7	1	13	30.3	32.2
8	1	13	0.0	13.2
9	1	13	41.2	40.4
10	1	13		

Table IX.

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