STRUCTURAL STUDIES
OF THE
BONDING
IN SOME
CYCLIC DIENE AND TRIENE COMPLEXES
OF
TRANSITION METAL IONS

A thesis submitted for the degree of
Doctor of Philosophy of the University of London

by

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ABSTRACT

π-cyclopentadienyl 1-phenyl-cyclopentadiene cobalt crystallizes as orthorhombic needles with $a = 29.64$ Å, $b = 7.70$ Å, $c = 10.68$ Å; the spacegroup is Pbca. A three-dimensional single-crystal X-ray structural analysis has been completed in which R has converged to 0.089 for 815 independent reflexions. The cyclopentadiene ligand is linked to the cobalt via one π- and two σ-bonds as is evidenced by the conformation of the ligand and detailed carbon-carbon bondlengths (average e.s.d. 0.03 Å). The phenyl group occupies the exo- rather than the endo- site suggested by spectroscopic techniques.

π-cyclopentadienyl hexakis(trifluoromethyl)benzene rhodium crystallizes in spacegroup $P2_1/c$ with $a = 9.48$ Å, $b = 12.59$ Å, $c = 17.79$ Å, $\beta = 114.75^\circ$. A three-dimensional structural investigation based on 2119 reflexions shows that the benzene ring is present in a non-planar conformation with only four of the six carbon atoms involved in bonding to the rhodium ion (the remaining two being approximately 1 Å further removed from the central metal). Although the reliability factor has reduced to the value 0.096, the difficulty of making a reasonable approximation for the librational motions of the six trifluoromethyl groups has resulted in some systematic errors which preclude any detailed discussion of carbon-fluorine bondlengths.

Octafluorocyclohexa-1,3-diene iron tricarbonyl crystallizes as large orthorhombic plates by sublimation at -5°C/760 mm.; the lattice parameters are $a = 13.49$ Å, $b = 6.92$ Å, $c = 11.89$ Å; the spacegroup is Pcam. A three-dimensional analysis of 666 independent reflexions has converged to a reliability index $R = 0.057$, making this structure the most accurate determination yet reported for an organo-metallic complex. The cyclohexadiene ring is again distorted from planarity, indicating some degree of localized metal-carbon interaction. All bondlengths have e.s.d.'s less than 0.015 Å.

The conditions favouring localized carbon-metal interaction in systems containing a formal butadiene residue are discussed in the light of these three structural analyses and a comparison made with other known structures of this type.

A brief introduction to organometallic chemistry prefaces the work, and a chapter on simple crystallographic methods is included.

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DEDICATION

To my parents,
in gratitude for their help
and encouragement.

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CHAPTER I

ORGANO-METALLIC COMPLEXES OF THE TRANSITION METALS

1.1. A Classification of Organometallic Compounds

The complexes formed between organic ligands and transition metals may be subdivided into groups according to the chemical nature of the ligand, the nature of the bonding between metal and ligand, or both. For the purpose of the present studies, the following five groups allow the most convenient method of classification.

a). σ-bonded alkyls and aryls

The organic ligand is bonded to the metal by a simple σ-bond, and there is no significant double-bond character in the metal-ligand linkage. Compounds of this group have wide variations in properties, but the simple metal alkyls, such as tetramethyltitanium or diethylnickel, are extremely unstable and are only isolable under an inert atmosphere in apparatus cooled to ca. -80°C. The stability of alkyls can be greatly enhanced by providing strong-field ligands on the metal. Thus, tricarbonyl-π-cyclopentadienylmolybdenum ethyl is stable for hour-long periods at room temperature, and trans-bis (tri-n-propylphosphine) platinum methyl iodide is completely air-stable at temperatures up to, and probably above, 80°C. Chatt and Shaw (1959) have discussed the stability of phosphine-platinum alkyls and conclude that the large splitting of the ligand-field, brought about by the phosphine ligands, increases the energy of the lowest non-bonding orbital and decreases that of the highest bonding orbital to such an extent as to inhibit the usual mechanism for decomposition involving the promotion of an electron from a bonding to a non-bonding orbital.

b). Complexes in which the carbon-metal σ-bond is greatly enhanced by simultaneous π-bonding between the two centres

This group includes the carbonyls, cyanides, isonitriles and acetylides. In all these complexes there are filled non-bonding d-orbitals of the metal which are of appropriate symmetry to overlap with fairly low-lying π-antibonding orbitals on the ligand. The excess charge associated with the metal after formation of the "initial" carbon-metal σ-bond, is immediately relieved by d-π^* back-donation. The resulting "synergic interaction" between σ-donation and π-back-donation results in maximum stabilization of such species as $Mo(CO)_6$ and $(Fe(CN)_6)^{4-}$.

c). Complexes of olefins and non-conjugated di-olefins are discussed in Section 1.2.

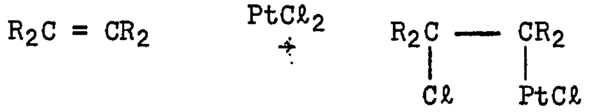
d). Complexes of conjugated olefins are introduced in Section 1.4. and form the basis for the crystallographic studies in this thesis.

e). Complexes of π-arene and related non-classical systems are considered in Section 1.3.

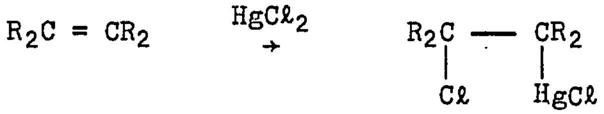
1.2. Olefin and Non-Conjugated Diolefin Complexes of Transition Metals

The chemistry of organo-metallic compounds began when, by treatment of a boiled ethanolic solution of chloroplatinic acid with potassium chloride, Zeise (1827) isolated a compound of formula

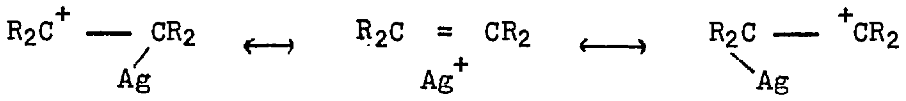
$KPtC\ell_3.C_2H_4.H_2O$. This, and the related complex $(PtC\ell_2.C_2H_4)_2$ were the only known organo-metallic compounds for some forty years, until Birnbaum (1868) reported the preparation of higher homologues of Zeise's salt up to the amylene complex. The first diolefin-metal complex was not prepared until 1908 when Hofmann and von Narbutt suggested that the formation of dicyclopentadieneplatinum dichloride, $C_{10}H_{12}PtC\ell_2$, could be explained in terms of the "platination" of a double bond:-

i.e.

$$R_2C = CR_2 \xrightarrow{PtC\ell_2} \underset{C\ell}{R_2C} - \underset{PtC\ell}{CR_2}$$

\- in a manner entirely analogous to the known mercuration reaction:-


$$R_2C = CR_2 \xrightarrow{HgC\ell_2} \underset{C\ell}{R_2C} - \underset{HgC\ell}{CR_2}$$

Little progress was made for some years, and as late as 1936, Kharasch and Ashford formulated $(C_2H_4PtC\ell_2)_2$ with two σ-bonded ethylene bridges between the two platinum atoms. Winstein and Lucas (1938) considered the resonance-stabilization of silver-olefin complexes between the three canonical forms:-


$$R_2\overset{+}{C} - \underset{Ag}{CR_2} \longleftrightarrow \underset{Ag^+}{R_2C = CR_2} \longleftrightarrow \underset{Ag}{R_2C} - {}^{+}CR_2$$

Dewar (1946) and Walsh (1947) later postulated that the π-electron pair in ethylene could donate to the metal in a way similar to the lone-pairs in ammonia or water. Dewar (1951) finally developed a molecular-orbital treatment for silver-olefin complexes whereby overlap of π-electrons with free metal orbitals was supplemented by the overlap of filled d-orbitals on the metal with antibonding orbitals on the olefin. This concept was extended by Chatt and Duncanson (1953) to include olefin-platinum complexes. A normal donor link is formed by donating π-electrons from the olefin into a dsp^2 hybrid orbital on the platinum. Since this, according to the Pauling Electroneutrality Rule, places too much charge on the metal, back-donation from occupied metal d- or dp-hybrid orbitals into the antibonding orbital on the olefin is used to balance charge distribution. This, in turn, induces the "synergic interaction" between forward $\pi \rightarrow dsp^2$ and back $pd \rightarrow \pi^*$ donation (in a way similar to the carbonyls, etc., Section 1.1). Figure 1.1 shows the scheme involved, and it is apparent that the olefin must lie perpendicular to the plane of the dsp^2 hybrid orbitals in order to attain maximum overlap for both π-bonding and back-donation.

This theory of bonding is in keeping with the slight lowering of $C = C$ stretching frequencies in the infra-red (ca. 50 cm^{-1} for olefin-silver and ca. 150 cm^{-1} for olefin-platinum complexes) and the proposed orientation of the olefin has been confirmed by X-ray crystallographic studies.

By virtue of the two forms of overlap with the metal, the olefin is a strong field ligand and, as such, is able to stabilize low valence states of metals. The chelating diolefins (that is, olefins with two non-conjugated double bonds in stereochemically acceptable positions to overlap with two of the hybrid orbitals of the metal coordination

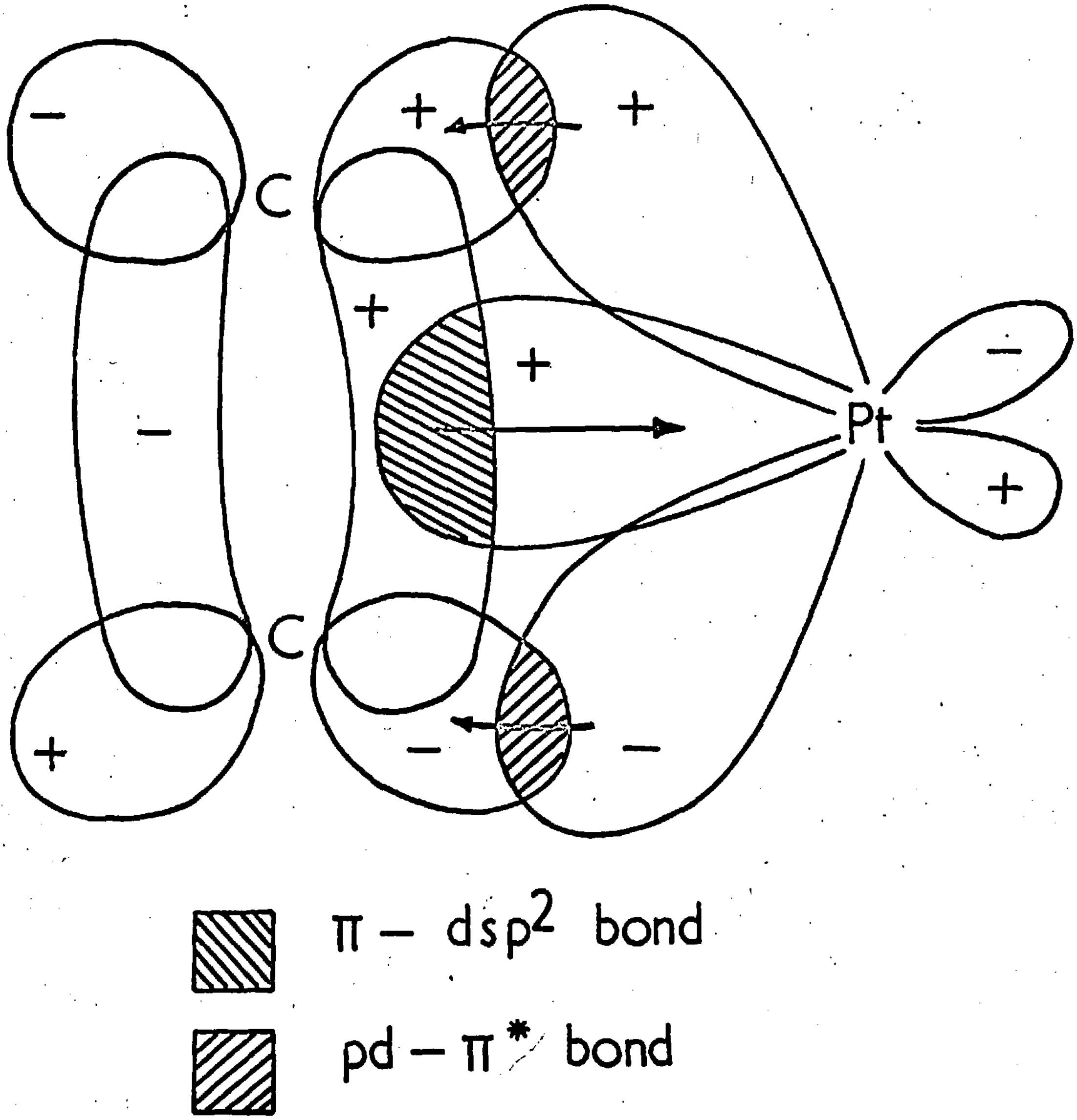


Figure 1.1
The Synergic Interaction between Forward Bonding and Back-Donation in Platinum-Olefin Complexes.

sphere) are particularly valuable in this respect. Thus Rh(+1) is stabilized in such complexes as $(C_8H_{12}RhC\ell)_2$, $(\text{nor-}C_7H_8RhC\ell)_2$ and $(C_8H_8RhC\ell)_2$, Re(+2) in $(C_{10}H_{12})\ ReC\ell_2$, Ru(+2) in $(\text{nor-}C_7H_8RuC\ell_2)_n$, and Ni(0) in (C_8H_{12}) Ni and $(C_8H_8Ni)_n$. Olefin complexes are easily made for the elements Ni, Cu, Ru, Rh, Pd, Re, Pt and Hg and can be prepared, if stabilized by other strong field ligands, for V, Cr, Mn, Fe, Co, Mo, W, Os and Ir.

Cramer (1964) has suggested, on the basis of proton magnetic resonance studies at various temperatures, that the ethylene ligands in $\pi - C_5H_5\ Rh\ (C_2H_4)_2$ are rotating and has proposed a scheme whereby the ethylene molecule, in this particular complex, can have strong forward bonding characteristics and a much weaker type of back donation.

1.3. Complexes of π-Arene and Related Non-Classical Systems

Although cyclopentadiene was known to form alkali metal salts, i.e. KC_5H_5 and NaC_5H_5, these are ionic and highly air- and water-sensitive.

Kealy and Pauson (1951) and Miller, Trebboth and Tremaine (1952) discovered, by widely differing routes, that iron also formed a cyclopentadienyl complex:-

$$2C_5H_5MgX + FeX_2 \rightarrow (C_5H_5)_2Fe + 2\ MgX_2$$

$$2C_5H_6 + Fe \xrightarrow{300^\circ C} (C_5H_5)_2Fe + H_2$$

The product, however, was not air-sensitive, was thermally stable beyond 400°C and was, in all respects, completely unlike all known organo-transition metal complexes. A "sandwich" structure, postulated for "ferrocene" by Wilkinson, Rosenblum, Whiting and Woodward (1952) and by Fischer and Pfab (1952), was soon confirmed by a series of crystallographic studies culminating in that by Dunitz, Orgel and Rich (1956). The iron atom is sandwiched between two delocalised π-C_5H_5 rings which are staggered (i.e. the molecule processes D_{5d} symmetry). Corresponding complexes of the first row transition metals from titanium to nickel were prepared and found (except for ionic manganocene) to be isomorphous. Ruthenocene, $(\pi\text{-}C_5H_5)_2Ru$, was shown by Hardgrove and Templeton (1959) to be in the eclipsed configuration, i.e. D_{5h} symmetry. This anomaly was explained in terms of the balance between carbon-carbon repulsions between the rings and intermolecular forces.

Following the discovery of the bis-π-cyclopentadienyls, Fischer and Hafner (1955) prepared the complex $(\pi\text{-}C_6H_6)Cr$, iso-electronic with ferrocene, which is air-sensitive but thermally very stable. It might be expected that the iso-electronic series be continued to include $(\pi\text{-}C_7H_7)_2$ Ti, but bis-π-tropyliene complexes are not isolatable presumably because:-

(i) the formal +1 charge of the tropylium ligand requires the metal to attain an oxidation state of -2, and

(ii) X-ray structural analyses indicate that the constant feature in sandwich complexes is the metal-carbon distance, <u>not</u> the perpendicular metal-ring distance.

This results in the possible $(\pi\text{-}C_7H_7)_2$ M complexes having carbon-carbon contacts considerably within the van der Waals' diaimeter for carbon. Although the bis-π-tropylium complexes are forbidden on purely steric grounds, mono-tropylium complexes (in common with mono-π-cyclopentadienyl and mono-π-benzene complexes) are extant, the first reported being π-$C_7H_7Mo(CO)_3BF_4$ (Dauben and Hannen, 1958) and π-C_7H_7Vπ-C_5H_5 (King and Stone, 1960). A simple molecular orbital treatment shows that the π-C_5H_5 ion has six electrons in orbitals available for bonding to the metal ion (see Figure 1.2) The a orbital is of correct symmetry to combine with the metal d_{z^2} (or $d_{z^2}s$ hybrid) orbital and the doubly degenerate $e_1^{\pm}$ orbitals can combine with the d_{xz} and d_{yz} orbitals of the transition metal. This scheme also applies, of course, to the six electrons in the π-benzene and π-tropylium systems.

Amongst other non-classical systems,the π-cyclohexadienyl system, first reported in π-$C_6H_7Mn(CO)_3$ (Winkhaus and Wilkinson, 1960) deserves special note since it is an intermediate in a large number of organic reaction mechanisms. The π-allyl, π-$C_3H_5^-$, system is well known, and the crystal structure of π-allyl palladium chloride, (π-$C_3H_5PdCl)_2$ has been reported (Rowe, 1962). The related cyclic π-cyclopropenium, π-$C_3H_3^+$, system has only recently been reported (Gowling and Kettle, 1964) and is not well characterised.

1.4. Complexes of Conjugated Olefins

The most important conjugated olefinic ligands, in order of increasing number of carbon atoms (n), are:-

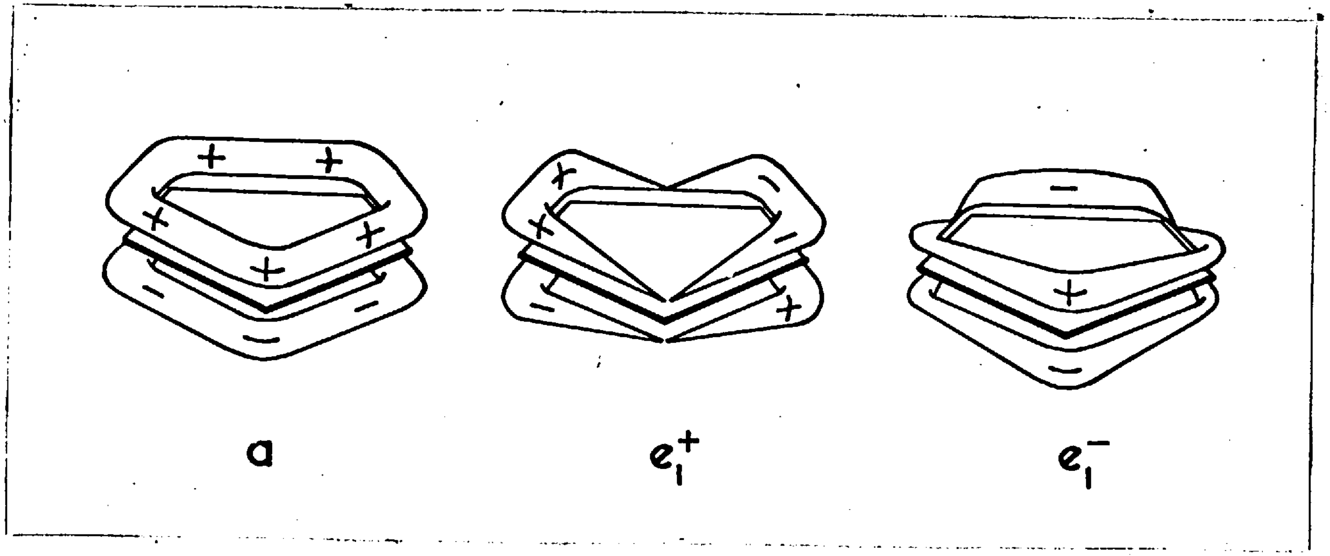


Figure 1.2. The Bonding Orbitals of the π-Cyclopentadienyl Ligand.

n = 4	butadiene cyclobutadiene
n = 5	cyclopentadiene cyclopentadienone
n = 6	cyclohexadiene benzene
n = 7	cycloheptatriene cycloheptatrienone
n = 8	cyclo-octatetra-ene

The first transition metal complex prepared from a conjugated olefin was butadiene iron tricarbonyl (Reilheu, Gruhl, von Hessling and Pfrengle, 1930) and the butadiene ligand was later used in preparing a series of organo-platinum complexes (Gelman, 1947). Since then, a large number of butadiene complexes have been reported, including $(C_4H_6)_2\ Mo(CO)_2$, $((C_4H_6)Co(CO)_2$, π-$C_5H_5 .\ V\ .\ C_4H_6(CO)_2$ and π-$C_5H_5Mn(C_4H_6)(CO)$. (Fischer and Werner, 1963).

Longuet-Higgins and Orgel (1956) postulated that cyclobutadiene, which was then unknown, could be stabilized by bonding to a transition metal. This prediction was confirmed when the complexes $(C_6H_5)_4\ C_4\ Fe(CO)_2$ (Hubel et al. 1959), $(CH_3)_4\ C_4\ NiC\ell_2$ (Criegee and Schroder, 1959) and $(C_4H_4Ag)NO_3$ (Avram et al. 1959) were prepared. X-ray structural investigations of the iron (Dodge and Schomaker, 1960) and nickel (Dunitz et al. 1962) complexes indicate that the cyclobutadiene ring is completely delocalized in these compounds and the proton magnetic resonance signal from $(C_4H_4Ag)NO_3$ has been shown to occur as a single peak at $\tau = 2{\cdot}7$ (Keller, 1962).

Cyclopentadiene complexes are discussed in chapter III, but these, along with cyclopentadienone and cyclohexadiene complexes, were all believed to bond to the metal via two π-bonds.

Benzene complexes were believed to contain delocalized benzene rings and, although an early structural analysis (Jellinek, 1960) indicated localized bonding (i.e. only D_{3h} symmetry), a more thorough investigation (Cotton, Collase and Wood, 1963) indicates that there is, in fact, strict D_{6h} symmetry in the molecule.

The first cycloheptatriene complex, prepared by Abel, Bennet and Wilkinson (1958), was cycloheptatriene molybdenium tricarbonyl, $C_7H_8Mo(CO)_3$. This compound has been shown, by a crystallographic structure determination (Dunitz and Pauling, 1960) to have a planar triene skeleton with apparently localized double-bonds.

Cyclo-octatetra-ene has been shown by X-ray methods (Kaufman et al., 1948) and electron diffraction (Bastiansen et al., 1957) to have a non-planar tub conformation with localized double-bonds and this conformation is retained in the silver complex $(C_8H_8Ag)NO_3$ (Mathews and Lipscomb, 1958). However, the complexes $C_8H_8Fe(CO)_3$ and $(OC)_3Fe\,C_8H_8Fe(CO)_3$ (Dickens and Lipscomb, 1962) show two new conformations - a dihedral and a chair form respectively.

This thesis is directed towards investigating the bonding of transition metal ions to (cyclic) conjugated olefinic systems by studying the detailed geometry of a cyclopentadiene, a benzene, and a cyclohexadiene complex. Other crystallographic studies are considered in the light of these investigations and a discussion of factors affecting conjugated olefin - metal bonding constitutes Chapter VI.

CHAPTER II

THE CRYSTALLOGRAPHIC METHOD

(For explanation of any symbols see Appendix, Section 2.9.)

2.1. The Crystal and Reciprocal Lattices

A one-dimensional lattice consists simply of a row of regularly spaced points; a two-dimensional lattice (or 'net') is composed of an evenly spaced array of rows; a three-dimensional lattice results from the even spacing of a series of (identical) nets. The crystal lattice therefore consists of a regular, periodic, three-dimensional array of lattice points. Since the crystal itself results from the repetition (in three dimensions) of the unit cell, in such a way as to fill space completely, there is one lattice point per unit cell. The unit cell may now be defined in terms of its sides a, b, c and angles α, β, γ, where a, b, c are now the distances between successive lattice points along the x, y, z axes respectively. α, β, γ are the angles between the axes y and z, x and z, x and y respectively.

An infinite number of stacks of planes can be drawn through a crystal (indeed, an infinite number of stacks of identical orientation and spacing, each displaced from the previous stack by an infinitesimal distance, are possible). If the zeroth member of a stack passes through a lattice point (taken as unit-cell coordinate o,o,o), then the Miller indices $(h\ k\ \ell)$ of the stack are defined as the reciprocal of the intercepts of the first member of the stack on the x, y, z axes.

e.g. The stack whose first member has intercepts a/4 b/3 c, has the Miller indices 431. The higher the Miller indices for a stack of planes, the closer together are the constituent planes. Thus, even this simple description introduces the idea of reciprococity, and this becomes so convenient (vide infra) that the concept of a reciprocal lattice becomes invaluable.

The reciprocal lattice can be constructed by drawing a line from the origin normal to each stack of planes ($h\ k\ \ell$). A point on this line, at a distance $1/d_{hk\ell}$ from the origin, corresponds to the reciprocal lattice point $h\ k\ \ell$. The reciprocal lattice therefore consists of a regular three-dimensional array of points. New axes are defined:

a* - perpendicular to the bc plane,
b* - perpendicular to the ac plane,
c* - perpendicular to the ab plane.

a*, b*, c* are also used to signify the separation of successive lattice points in their respective directions. The angles α^*, β^*, γ^* are now used to define the relative orientation of the three reciprocal axes.

The mathematics of the transformation from real to reciprocal space are identical with the Fourier transform. The Fourier transform of a unit cell is the diffraction pattern which would be produced by the (single) cell. The Fourier transform of an infinite, three dimensional array of unit cells (i.e. a crystal) is its weighted reciprocal lattice and equivalent, from the practical viewpoint, to the diffraction pattern of the crystal considered.

All general relationships between real and reciprocal space are shown in Appendix, Section 2.9. The expressions shown are general, and therefore reduce to much simpler form for crystals with symmetry higher than triclinic.

2.2. Measurement of Unit Cell Parameters

The dimensions of crystallographic axes may be determined directly from rotation or cone-axis photographs. Weissenberg and precession photographs are direct photographs of the reciprocal lattice (in the latter case, photographs of the undistorted reciprocal lattice) and, consequently, any measurements on photographs obtained by these methods lead to the reciprocal (rather than the real) lattice parameters. However, the relationships between the two systems are well understood, and this presents no real problem.

Unit cell parameters are obtained from the various photographs by using the following expressions (each of which is no more than a specific statement of the Bragg equation, modified to fit the geometry of the camera).

(i) Rotation Method

$$\text{Axis length (Å)} = \frac{n\lambda}{\sin(\tan^{-1} p/r)}$$

r = camera radius (mm.)

p = separation (mm.) of the n^{th} from the zeroth layer line.

λ = wavelength of radiation used (Å)

(ii) Cone-axis Method

$$\text{Axis-length (Å)} = \frac{n\lambda}{\cos\mu - \cos(\tan^{-1} r/s)}$$

μ = precession angle

s = crystal to film distance (mm.)

r = radius of ring due to reflexions from the n^{th} reciprocal lattice layer.

(iii) Weissenberg Method

$$d^* = \frac{2 \sin (0.2\sqrt{5}.\ p)}{n\lambda}$$

p = distance between the $+n^{th}$ and $-n^{th}$ reflexions on the d* axis of a zero-layer photograph.

The above relationship pre-assumes a geometry and mechanism whereby a camera of radius $90/\pi$ mm. has a gearing between rotation of crystal and traverse of camera such that a 2° rotation is accompanied by a 1mm. traverse.

(iv) Precession Method

$$d^* = \frac{p}{2nF\lambda}$$

p = distance (mm.) between $+n^{th}$ and $-n^{th}$ reflexion along the d* axis of the photograph.

F = crystal to film distance (= 60 mm. in camera used).

Weissenberg and precession data give a measure of the reciprocal lattice angles $\alpha^*, \beta^*, \gamma^*$ which are directly related to the required angles α, β, γ.

Once all the cell parameters have been determined, the volume of the unit cell is calculated and, using the relationship:-

$$\rho = \frac{nM}{NV}$$

where ρ = density (gm.cm.$^{-1}$) of compound

N = Avagadro number;

M = molecular weight of compound;

V = volume (cm.^{3}) of unit cell;

n = number of molecules per unit cell.

the molecular weight of the compound is checked and the number of molecules per unit cell (n) determined.

There are six crystal systems:-

Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

The trigonal system can be expressed in terms of rhombohedral axes ($a = b = c$, $\alpha = \beta = \gamma < 120^\circ$, $\neq 90^\circ$) or hexagonal axes ($a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) and consequently is considered as a sub-group of the hexagonal class.

The crystal system is easily determined by inspection of the unit cell parameters and a careful study of the symmetry of the reciprocal lattice photographs.

A study of the systematic absences in the various zones shows the various symmetry elements present. For example the conditions that the $h\ k\ \ell$ reflexions are only present for $\{h + k + \ell\} = 2n$, $\{h + k\} = 2n$ indicate body-centering and C face-centering respectively; $h\ 0\ \ell$ present for $h = 2n$ (only) shows an a-glide perpendicular to b; the halving of a zero-layer axis indicates a 2_1 axis unless subsidiary conditions are present.

Finally, when all systematic absences have been located, the space-group of the crystal may be determined either (i) uniquely or (ii) as a number of possibilities (generally with or without a centre of symmetry) from which the true space group will emerge only as refinement proceeds.

2.3. The Structure Factor

When an X-ray quantum interacts with an electron, the electromagnetic field associated with the X-ray forces the electron into oscillation. The electron now becomes a source of radiation, resulting in the effective scattering of the incident radiation. Since atoms consist partly of electrons, it follows that any material will scatter X-rays. (In fact the charged nuclei also interact with X-rays, but this effect is some orders of magnitude less important). However, only materials with periodic structure will scatter radiation coherently.

The "weight" with which an element scatters X-rays is related to the atomic scattering factor (f). This is not constant, but is a function of the angle of diffraction (the Bragg angle, θ). At small θ-values, all electrons in the atom scatter approximately in phase, and the atomic scattering factor approximates very closely to the atomic number, or, more strictly, the number of extranuclear electrons. At higher angles of diffraction, interference between X-rays scattered from the various electrons in the atom results in the graphs of f versus $\sin\theta/\lambda$ showing their characteristic fall-off with increasing θ.

The application of fundamental diffraction theory shows that the arrangement of atoms in a unit cell dictates the magnitude, and phase, of the coherent scattering from the planes $h\ k\ \ell$. The intensity of the diffraction peaks which are experimentally observed are directly related to the modulus of the structure factor (the so-called structure amplitude, $|F(hk\ell)|$). The structure factor can be calculated knowing the positions of the n atoms of the unit cell:-

$$F(hk\ell) = \sum_{j=1}^{j=n} f_j \exp 2\pi i\,(hx_j + ky_j + \ell z_j)$$

where x_j, y_j, z_j are the fractional coordinates, and f_j is the atomic scattering factor (at the appropriate Bragg angle $\theta_{hk\ell}$) for the j^{th} atom.

The expression for the structure factor may be simplified by the use of trignometric expressions since there are usually symmetry-related equipoints in the cell. For example, every centrosymmetric spacegroup has an atom at $-x, -y, -z$ identical to that at x,y,z. The contributions from the two atoms are:-

$$f \exp 2\pi i\,(hx + ky + \ell z) \quad \text{and}$$

$$f \exp 2\pi i\,(-hx - ky - \ell z)$$

These are easily compounded by virtue of the identity $\exp(ix) + \exp(-ix) = 2\cos x$.

Thus, for the centrosymmetric case, the expression reduces to a summation over only half the atoms in the unit cell.

$$F(hk\ell) = 2 \sum_{j=1}^{j=n/2} f_j \cos 2\pi(hx_j + ky_j + \ell z_j)$$

For all non-centrosymmetric spacegraphs the calculation is made in two parts:-

$$F(hk\ell) = A(hk\ell) + iB(hk\ell)$$

The structure factor thus has a phase, which, by use of an Argand diagram is shown to be given by

$$\phi = \tan^{-1} B/A$$

The magnitude of the structure factor is easily determined from the observed diffraction data, but the phase of the structure factor cannot directly be determined. This results in the so-called "Phase Problem", and is the reason why it is not possible to determine a crystal structure directly from the observed structure amplitudes.

For non-centrosymmetric spacegroups, the phase angle of a reflexion is continuously variable and may have any value (ϕ) such that $-\pi < \phi < \pi$. For centrosymmetric spacegroups, the phase of a given reflexion $hk\ell$ is no longer continuously variable, since the contribution from the atom at x,y,z is mathematically combined with that from the identical atom at -x, -y, -z and the imaginary component of F disappears. The phase now required is given by $\phi = \tan^{-1} 0/A$ and $\phi = 0$ or $\pm\pi$.

Unfortunately, the equation

$$F(hk\ell) = \sum f_j \exp 2\pi i\ (hx_j + ky_j + \ell z_j)$$

is pertinent only to stationary atoms. In fact, atoms undergo thermal vibrations of frequency ~ 10^{13} c.p.s. Since X-rays have a frequency of ~10^{18} c.p.s., the time-averaged position of the atom is actually found, and the atom has considerable volume. This can be allowed for by making the substitution $f = f_o \exp(-B \sin^2 \theta/\lambda^2)$ where B is termed the isotropic temperature factor and is related to the root mean square displacement ($\bar{U}^2$) of the atom from its mean position by $B = 8\pi^2 \bar{U}^2$.

In many crystals, particularly molecular crystals, the atomic vibrations are decidedly non-isotropic and this can be allowed for by replacing the isotropic temperature factor, B, by the anisotropic temperature factors b_{ij}. The substitution is now:-

$$f = f_o \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{23}k\ell + b_{13}h\ell + b_{12}hk)$$

This equation relates to the major, median and minor axes of the ellipsoid of vibration, and its orientation with respect to the crystallographic axes.

2.4. Intensity Photographs and their Correction for Physical and Geometric Factors.

The position of reflexions on a film is a function of the unit cell parameters, the geometry of the camera and the wavelength of the radiation employed, but the intensities of the various reflexions are related to the structure amplitude thus:-

$$\text{Intensity } (h\ k\ \ell) = K.L\,(h\ k\ \ell).\ p(h\ k\ \ell).\ |F(h\ k\ \ell)|^2$$

where $L(h\ k\ \ell)$ = Lorentz correction

$p(h\ k\ \ell)$ = polarization correction

K = experimental constant (but equal for all reflexions in a given zone).

The polarization factor is identical for all camera geometries. It depends only on the angle of diffraction $\theta(h\ k\ \ell)$, the relationship being:-

$$p(h\ k\ \ell) = \tfrac{1}{2}(1 + \cos^2\theta(h\ k\ \ell))$$

This is easily understood when it is remembered that the incident (non-polarized) radiation will not, on reflection, be polarized perpendicular to the stack of planes $(h\ k\ \ell)$, but will be polarized parallel to this direction.

The Lorentz factor, however, is a measure of the relative time for which crystal and detector are in suitably related positions for the reflexion from the plane considered to be recorded. The form of the Lorentz correction is very different for the various geometries of cameras.

For Weissenberg motion the expression is:-

$$L(h\,k\,\ell) \quad = \quad K' \,/\, \sin \tau(h\,k\,\ell)$$

where K' is a constant (common to all reflexions in a given zone, and hence eventually incorporated in the overall experimental constant K). $\tau(h\,k\,\ell)$ is a film coordinate and is directly proportional to the perpendicular distance (s mm.) of the $h\,k\,\ell$ reflexion from the centre line of the cylindrical film. For a camera of radius $90/\pi$ mm., 2s (in mm.) is numerically equal to τ $(h\,k\,\ell)$ in degrees.

For precession motion with universal-joint suspension (as used) the correction is so complicated that it is always done graphically (or by computer). The expression involved is:-

$$L(h\,k\,\ell) \quad = \quad \frac{\left[1 + \tan^2\mu\sin^2(\tau+\eta)\right]^{-1} + \left[1 + \tan^2\mu\sin^2(\tau-\eta)\right]^{-1}}{2\cos\mu\,\sin\mu\,\sin\nu\,\sin T}$$

where $\eta \quad = \quad \sin^{-1} \dfrac{(\sin\nu\,\sin T)}{(2\sin\theta\,(h\,k\,\ell))}$

μ = precession angle; ν, T, τ are all angular film coordinates.

The intensities of the various crystallographic zones are measured and corrected for Lorentz and polarization effects. Each zone is now on its own arbitrary scale, but all data are placed on a common scale by comparison of common reflexions (e.g. $h\,0\,\ell$ and $h\,k\,0$ zones can be scaled together by comparing the relative magnitudes of $h\,0\,0$ reflexions). Finally a set of scaled, corrected intensities is available which is related to the structure factors for the proposed (correct) model, by:-

$$k \mid F_{obs} \mid \quad = \quad \mid F_{calc} \mid$$

The value of k is determined by trial and error (using refinement techniques), and is one of the variables continually adjusted during the course of refining the structure.

As refinement (q.v.) proceeds, it is often noticed that some of the intense low order reflexions are showing a much worse fit with the calculated values than are any other reflexions and that the observed value of these planes is consistently smaller than the calculated. This is usually due to extinction, of which there are two types:-

(i) Primary Extinction: attenuation of both main and emergent beams results from multiple reflection of rays from a given stack of planes. The X-ray undergoes a phase change of $\pi/2$ on reflection, so that twice-reflected rays are π radians out of phase with the main beam and thrice-reflected rays are π radians out of phase with the main reflexion. Hence the emergent beam is weaker than theoretically calculated. The effect is only noticeable for the intense low-order reflexions.

(ii) Secondary Extinction: the incident (main) beam is continuously attenuated as it penetrates the crystal simply due to the upper planes in the crystal reflecting some of the rays at a Bragg angle. Again, the effect is only noticeable for the intense, low-order reflexions.

Extinction is due to the "perfection" of the crystal examined and can be reduced only by ensuring that the crystal approaches the "ideally imperfect" state. This means shattering the crystal into a mosaic-like mass in which no stack of planes is of appreciable height without some (small, but finite) discontinuity occurring. This mosaicicity may be achieved by quickly immersing the crystal in liquid nitrogen. Theoretical allowance for extinction is difficult and planes whose observed structure amplitudes are thought to be erroneous due to this cause are usually simply removed from the refinement procedure. (It is customary to include the calculated values of such reflexions into any Fourier syntheses which are required.)

The other possible cause of error is absorption. X-rays are actually absorbed as they pass through matter. It is possible, though sometimes extremely difficult, to calculate the absorption corrections which must be applied to each of the observed structure amplitudes. Corrections for spherical and cylindrical specimens are well documented but for other shapes the corrections are very laborious. However, it is usually possible to ignore absorption corrections provided that small crystals (< 0.2 mm. in diameter) are used in the analysis, and provided that hard radiation is used when heavy metals are present. In the present studies molybdenum K_α radiation ($\bar{\lambda} = 0.7107$ Å) is far preferable to copper K_α ($\bar{\lambda} = 1.5418$ Å) because of the smaller degree of absorption.

2.5. The Fourier Synthesis and the Patterson Method for Solution of the Phase Problem.

The crystal is an ordered, three-dimensional array, and as such can be represented by a three-dimensional Fourier series. Since crystal-structure investigations are dependent on the scattering of X-rays by electrons, it is the electron density throughout the crystal which is described by the Fourier series. The electron density (ρ) at a point of fractional co-ordinates x, y, z can be calculated from:-

$$\rho\,(xyz) = \frac{1}{V} \sum_{h,\,k,\,\ell = -\infty}^{h,\,k,\,\ell = +\infty} \sum \sum F(hk\ell) \exp - 2\pi i(hx + ky + \ell z)$$

Since in the general case $F(hk\ell)$ is complex and:-

$$F(hk\ell) = A(hk\ell) + i\,B(hk\ell),$$

the above equation becomes:-

$$\frac{1}{V} \sum \sum \sum \big(A(hk\ell) + i\,B(hk\ell)\big)\big(\cos 2\pi(hx + ky + \ell z) - i \sin 2\pi(hx + ky + \ell z)\big)$$

However, Friedel's law states that for reflexions not near an absorption edge:-

$$F(hk\ell) = F(\bar{h}\bar{k}\bar{\ell})$$

The Fourier equation now reduces to:-

$$\rho(xyz) = \frac{2}{V}\Big[\frac{1}{2} F_{000} + \sum_{h=0}^{h=+\infty} \sum_{k=-\infty}^{k=+\infty} \sum_{\ell=-\infty}^{\ell=+\infty} A(hk\ell) \cos 2\pi(hx + ky + \ell z) + B(hk\ell) \sin 2\pi(hx + ky + \ell z)\Big]$$

The F_{000} term is halved because it is the only reflexion for which $hk\ell$ is itself $\bar{h}\bar{k}\bar{\ell}$.

Although, in theory, the Fourier summation must be from $-\infty$ to $+\infty$, in practice it is merely over all reflexions which have actually been observed. Due to this there is the "series termination effect" which sometimes manifests itself in a series of concentric peaks surrounding a heavy atom.

A two-dimensional Fourier synthesis can also be performed. For a two-dimensional electron density projection down, for example, the a- axis, only the $0k\ell$ structure factors are required:-

$$\rho(yz) = \frac{1}{A} \sum_{k=-\infty}^{k=+\infty} \sum_{\ell=-\infty}^{\ell=+\infty} \left(F(0k\ell) \exp - 2\pi\, i(ky + \ell z)\right)$$

This may be expanded as before.

If some of the atomic positions are known and some remain to be found, then a "difference" synthesis, using $\left(kF_{obs} - F_{calc}\right)$ as the Fourier coefficients is used to reveal the remaining atoms. This method also eliminates the ripples round a heavy atom due to the series termination effect.

When two Fourier series, each of which represents the electron density of a crystal, are multiplied together, then terms such as $F(hk\ell)\ F(\bar{h}\bar{k}\bar{\ell})$ occur. However, $F(\bar{h}\bar{k}\bar{\ell})$ is the complex conjugate of $F(hk\ell)$.

$$F(hk\ell)\ F(\bar{h}\bar{k}\bar{\ell}) = |F(hk\ell)|^2$$

The square of the structure amplitude is a phaseless quantity, and, further, is obtainable directly from the corrected intensity data.

It has been shown that a Fourier series using $|F(hk\ell)|^2$ as the coefficients gives information on the interatomic vectors. Whereas $\rho(xyz)$ has maxima at atomic positions, the Patterson synthesis, P(UVW), given by:-

$$P(UVW) = \frac{1}{V^2} \sum\sum\sum_{h,k,\ell = -\infty}^{h,k,\ell = +\infty} |F(hk\ell)|^2 \exp 2\pi i \, (hu + kv + \ell w)$$

$$\text{or:} \quad P(UVW) = \frac{2}{V^2}\left[\frac{1}{2} F_{000} + \sum\sum\sum_{h=o;k,\ell = -\infty}^{h,\ k,\ \ell = +\infty} |F(hk\ell)|^2 \cos 2\pi(hu + kv + \ell w)\right]$$

has peaks at the ends of vectors between atomic positions. For a unit cell containing n atoms there are n(n - 1) vectors linking these atoms. Whereas the volume of an atomic peak in a Fourier synthesis is equal to the number of electrons (Z) in the atom concerned, the volume of a Patterson peak is equal to the product of the number of electrons in each of the atoms related by the vector.

For example: a compound containing zinc, carbon and hydrogen will give rise to a Patterson synthesis in which there are peaks of relative volume 900 (Z(Zn) x Z(Zn)), 180 (Z(Zn) x Z(C)), 36 (Z(C) x Z(C)), 30 (Z(Zn) x Z(H)), 6 (Z(C) x Z(H)) and 1 (Z(H) x Z(H)). Unless there is severe overlap of zinc-carbon vector-peaks, all the zinc-zinc vectors will easily be located. These vectors can, by trial and error, be related to vectors between the possible equipoints in the (known) spacegroup. Thus, in the simplest case, if the zinc compound above was in spacegroup $P\bar{1}$ with equipoints x, y, z and -x, -y, -z. then zinc-zinc vectors would appear at the points UVW = ± (2x, 2y, 2z) only. The metal coordinates are immediately obtainable. The heavy atom will, in general, dictate the phases of the majority of the Bragg reflexions (particularly the strong ones) since the large number of electrons constituting the atom will scatter approximately in phase, whereas the residual light atoms will be scattering randomly and are unlikely to produce a "residual structure amplitude" large enough to offset that controlled by the heavy atom. The analysis starts with a Fourier phased only by the heavy atom and proceeds via structure factor calculations (phased by an increasing number of atoms) and Fourier syntheses (locating more and more atoms) until approximate positions are known for all atoms in the unit cell.

2.6. The Refinement of Atomic Coordinates.

Once Fourier methods have approximately located the atomic positions, these coordinates can, in principle, be refined to completion by a least-squares refinement procedure.

If each atom is in the (slightly erroneous) position x,y,z and its correct location is $x + \varepsilon_x$, $y + \varepsilon_y$, $z + \varepsilon_z$, then:-

$$F_{obs} = f(x + \varepsilon_x, y + \varepsilon_y, z + \varepsilon_z)$$

$$F_{calc} = f(x, y, z)$$

Assuming the deviations, ε, are not too large, then F_{obs} can be expanded by Taylor's Theorem:-

$$f(x + \varepsilon_x, y + \varepsilon_y, z + \varepsilon_z) = f(xyz)$$

$$+ \varepsilon_x \frac{\partial}{\partial x} f(xyz) + \varepsilon_y \frac{\partial}{\partial y} f(xyz) + \varepsilon_z \frac{\partial}{\partial z} f(xyz)$$

Define $\Delta = F_{obs} - F_{calc}$

$$\Delta = \varepsilon_x \frac{\partial}{\partial x} f(xyz) + \varepsilon_y \frac{\partial}{\partial y} f(xyz) + \varepsilon_z \frac{\partial}{\partial z} f(xyz)$$

But $f(xyz) = F_{calc}$

$$\Delta = \left(\varepsilon_x \frac{\partial}{\partial x} + \varepsilon_y \frac{\partial}{\partial y} + \varepsilon_z \frac{\partial}{\partial z} \right) F_{calc}$$

This equation is for one value of F_{calc}. Summing over all observed reflexions using a weighting scheme such that w(hkℓ) is the weight for the reflexion hkℓ, then Legendre's principle (stating that the best result is obtained by minimization of the weighted squares of the difference between observed and calculated values) leads to the starting equation:-

$$\sum_{hk\ell} w(hk\ell) \left(\Delta (hk\ell) \right)^2 =$$

$$\sum_{hk\ell} \sum_{j=1}^{j=n} w(hk\ell) \left\{ \left(\varepsilon_{xj} \frac{\partial}{\partial x_j} + \varepsilon_{yj} \frac{\partial}{\partial y_j} + \varepsilon_{zj} \frac{\partial}{\partial z_j} \right) F(hk\ell) \right\}^2$$

where $\sum_{hk\ell}$ indicates that each of the observed structure factors F(hkℓ) are considered and $\sum_{j=1}^{j=n}$ indicates that the deviations ε_{xj}, ε_{yj}, ε_{zj} of each of the atoms from its position x_j, y_j, z_j is being considered.

The above equation can be minimized by differentiating, in turn, with respect to ε_{x1}, ε_{y1}, ε_{z1}, ... ε_{xj}, ε_{yj}, ε_{zj} .... ε_{xn}, ε_{yn}, ε_{zn}, and setting each of the equations equal to zero. 3n equations are thus set by differentiation:-

$$\frac{\partial}{\partial\varepsilon_{x1}} \sum_{hk\ell} w(hk\ell) \left(\Delta(hk\ell)\right)^2 = 0 =$$

$$\sum_{hk\ell} \sum_{j=1}^{j=n} w(hk\ell) \left(2\cdot \frac{\partial F(hk\ell)}{\partial x_1}\right)\left(\varepsilon_{xj} \frac{\partial}{\partial x_j} + \varepsilon_{yj} \frac{\partial}{\partial y_j} + \varepsilon_{zj} \frac{\partial}{\partial z_j}\right) F(hk\ell)$$

etc.

After separating the variables (neglecting the summation over all hkℓ and replacing F(hkℓ) by F), the 3n normal equations are:-

$$\varepsilon_{x1} \left(\frac{\partial F}{\partial x_1}\right)^2 + \varepsilon_{y1} \left(\frac{\partial F}{\partial x_1}\right) \left(\frac{\partial F}{\partial y_1}\right) + \varepsilon_{z1} \left(\frac{\partial F}{\partial x_1}\right) \left(\frac{\partial F}{\partial z_1}\right) +$$

$$\varepsilon_{x2} \left(\frac{\partial F}{\partial x_1}\right) \left(\frac{\partial F}{\partial x_2}\right) + \varepsilon_{yz}\left(\frac{\partial F}{\partial x_1}\right) \left(\frac{\partial F}{\partial y_2}\right) + \ldots\ldots \varepsilon_{zn} \left(\frac{\partial F}{\partial x_1}\right) \left(\frac{\partial F}{\partial z_n}\right) = 0$$

$$\varepsilon_{x1} \left(\frac{\partial F}{\partial x_1}\right) \left(\frac{\partial F}{\partial y_1}\right) + \varepsilon_{y1}\left(\frac{\partial F}{\partial y_1}\right)^2 + \varepsilon_{z1} \left(\frac{\partial F}{\partial y_1}\right)\left(\frac{\partial F}{\partial z_1}\right) +$$

$$\varepsilon_{x2} \left(\frac{\partial F}{\partial y_1}\right) \left(\frac{\partial F}{\partial x_2}\right) + \varepsilon_{y2}\left(\frac{\partial F}{\partial y_1}\right) \left(\frac{\partial F}{\partial y_2}\right) + \ldots\ldots\ldots \varepsilon_{zn} \left(\frac{\partial F}{\partial y_1}\right) \left(\frac{\partial F}{\partial z_n}\right) = 0$$

$$\varepsilon_{x1}\left(\frac{\partial F}{\partial x_1}\right)\left(\frac{\partial F}{\partial z_1}\right) + \varepsilon_{y1}\left(\frac{\partial F}{\partial y_1}\right)\left(\frac{\partial F}{\partial z_1}\right) + \varepsilon_{z1}\left(\frac{\partial F}{\partial z_1}\right)^2 +$$

$$\varepsilon_{x2}\left(\frac{\partial F}{\partial z_1}\right)\left(\frac{\partial F}{\partial x_2}\right) + \varepsilon_{y2}\left(\frac{\partial F}{\partial z_1}\right)\left(\frac{\partial F}{\partial y_2}\right) + \ldots \; \varepsilon_{zn}\left(\frac{\partial F}{\partial z_1}\right)\left(\frac{\partial F}{\partial z_n}\right) = 0$$

$$\varepsilon_{x1}\left(\frac{\partial F}{\partial x_1}\right)\left(\frac{\partial F}{\partial x_2}\right) + \varepsilon_{y1}\left(\frac{\partial F}{\partial y_1}\right)\left(\frac{\partial F}{\partial x_2}\right) + \varepsilon_{z1}\left(\frac{\partial F}{\partial z_1}\right)\left(\frac{\partial F}{\partial x_2}\right) +$$

$$\varepsilon_{x2}\left(\frac{\partial F}{\partial x_2}\right)^2 + \varepsilon_{y2}\left(\frac{\partial F}{\partial x_2}\right)\left(\frac{\partial F}{\partial y_2}\right) + \ldots \; \varepsilon_{zn}\left(\frac{\partial F}{\partial x_2}\right)\left(\frac{\partial F}{\partial z_n}\right) = 0$$

$$\begin{array}{ccc} '' & '' & '' \\ '' & '' & '' \\ '' & '' & '' \\ '' & '' & '' \\ '' & '' & '' \end{array}$$

$$\varepsilon_{x1}\left(\frac{\partial F}{\partial x_1}\right)\left(\frac{\partial F}{\partial z_n}\right) + \varepsilon_{y1}\left(\frac{\partial F}{\partial y_1}\right)\left(\frac{\partial F}{\partial z_n}\right) + \varepsilon_{z1}\left(\frac{\partial F}{\partial z_1}\right)\left(\frac{\partial F}{\partial z_n}\right) +$$

$$\varepsilon_{x2}\left(\frac{\partial F}{\partial x_2}\right)\left(\frac{\partial F}{\partial z_n}\right) + \varepsilon_{y2}\left(\frac{\partial F}{\partial y_2}\right)\left(\frac{\partial F}{\partial z_n}\right) + \ldots \; \varepsilon_{zn}\left(\frac{\partial F}{\partial z_n}\right)^2 = 0$$

By solving these 3n normal equations, the 3n values for the deviations, ε, can be calculated.

However, atoms have temperature factors, and 4n normal equations are required to simultaneously refine positional and isotropic thermal parameters for n unrelated atoms.

Using the shorthand notation:-

$$X_1 \equiv \left(\frac{\partial F}{\partial x_1}\right) \quad Y_1 \equiv \left(\frac{\partial F}{\partial y_1}\right) \quad Z_1 \equiv \left(\frac{\partial F}{\partial z_1}\right) \quad B_1 \equiv \left(\frac{\partial F}{\partial B_1}\right)$$

$$X_2 \equiv \left(\frac{\partial F}{\partial x_2}\right) \quad Y_2 \equiv \left(\frac{\partial F}{\partial y_2}\right) \quad Z_2 \equiv \left(\frac{\partial F}{\partial z_2}\right) \quad B_2 \equiv \left(\frac{\partial F}{\partial B_2}\right)$$

$$'' \quad '' \quad '' \quad '' \quad '' \quad '' \quad '' \quad ''$$

$$X_n \equiv \left(\frac{\partial F}{\partial x_n}\right) \quad Y_n \equiv \left(\frac{\partial F}{\partial y_n}\right) \quad Z_n \equiv \left(\frac{\partial F}{\partial z_n}\right) \quad B_n \equiv \left(\frac{\partial F}{\partial B_n}\right)$$

The normal equations are now:-

$$\begin{array}{l}
\varepsilon_{x1} X_1^2 + \varepsilon_{y1} X_1Y_1 + \varepsilon_{z1} X_1Z_1 + \varepsilon_{B1} X_1B_1 + \ldots = 0 \\
\varepsilon_{x1} X_1Y_1 + \varepsilon_{y1} Y_1^2 + \varepsilon_{z1} Y_1Z_1 + \varepsilon_{B1} Y_1B_1 + \ldots = 0 \\
\varepsilon_{x1} X_1Z_1 + \varepsilon_{y1} Y_1Z_1 + \varepsilon_{z1} Z_1^2 + \varepsilon_{B1} Z_1B_1 + \ldots = 0 \\
\varepsilon_{x1} X_1B_1 + \varepsilon_{y1} Y_1B_1 + \varepsilon_{z1} Z_1B_1 + \varepsilon_{B1} B_1^2 + \ldots = 0 \\
\varepsilon_{x1} X_1X_2 + \varepsilon_{y1} Y_1X_2 + \varepsilon_{z1} Z_1X_2 + \varepsilon_{B1} B_1X_2 + \ldots = 0
\end{array}$$

etc.

A full-matrix refinement takes into account all terms in the normal equations, but "block-diagonal" matrix refinement ignores all cross-terms between atoms. The problem is thus reduced from solving a single determinant of rank 4n to solving n determinants of rank 4.

When the thermal motion of the atom is described by the anisotropic temperature factors b_{ij}, the above scheme again applies, but six terms are now used in describing the anisotropic thermal motion of each atom. Thus 9n normal equations are now required to be solved for the deviations, ε.

A full-matrix anisotropic refinement of n atoms requires the solution of a 9n-rank matrix, and can only be performed on the very latest computers. The usual approach to this problem is to neglect all cross terms between different atoms and also to neglect vibrational-positional cross terms for any atom. This results in the 9n-rank matrix being reduced to n matrixes of rank 6 for vibrational refinement and n matrixes of rank 3 for positional refinement. A further quantity which must be refined is the scalefactor k, which must be applied to the observed structure amplitudes in order to give the best fit with the refined structure. This increases the rank of the matrix to 9n + 1 (for anisotropic) and 4n + 1 (for isotropic) full-matrix refinement. In block diagonal refinement, a further 2 x 2 matrix is introduced to allow for the interaction between the scalefactor k and Q (the overall isotropic temperature for the model).

2.7. Geometric Calculations

Once the completely refined coordinates are available, the geometry of the molecule can be calculated. This is simply a direct application of three-dimensional Pythagoras' theorem when the unit cell has orthogonal axes, but can be much more complicated when such symmetry is absent. Both distances and angles are more simply calculated if all atomic coordinates are converted to Cartesian coordinates immediately. This is done by defining the mutually perpendicular axes a, b* and c sin β. Once all atomic coordinates have been converted to this system, Pythagoras' theorem and the cosine formula ($a^2 = b^2+c^2-2bc \cos A$)

can be used to determine all distances and angles.

Another calculation often necessary is the determination of the planarity (or otherwise) of a group of atoms. Once again, all atomic coordinates are converted to Cartesian coordinates using the orthogonal axes a, b* and c sin β.

A plane is defined by an equation of the type:-

$$px + qy + rz + d = 0$$

where x, y, z are coordinates of any point in the plane, p, q, r are the direction cosines (d.c.'s) of the normal to the plane, and d is the perpendicular distance of the origin of the coordinate system from the plane.

The plane associated with a set of weighted points in three-dimensional space is best described such that the sum of the (weighted) squares of the deviations of the points from this plane is minimized. The deviation (H) of a point x_n, y_n, z_n from the plane $px + qy + rz + d = 0$ is given by

$$H = \frac{px_n + qy_n + rz_n + d}{(p^2 + q^2 + r^2)^{\frac{1}{2}}}$$

but since $p^2 + q^2 + r^2 = 1$ (Cartesian coordinates are being used) the quantity to be minimized is thus:-

$$\sum_n w_n H_n^{\ 2} = \sum_n w_n (px_n + qy_n + rz_n + d)^2$$

where w_n is the weight of the n^{th} point.

This equation is minimized by setting up the four normal equations, obtained by differentiating the above equation with respect to p, q, r and d, and equating to zero. Thus:-

$$\frac{\partial}{\partial p} \sum_n w_n H_n^{\,2} = \sum_n w_n (2x_n)(px_n + qy_n + rz_n + d)$$

etc.

The final normal equations are, therefore:-

$$\sum_n w_n (px_n^{\,2} + qx_ny_n + rx_nz_n + d) = 0$$

$$\sum_n w_n (px_ny_n + qy_n^{\,2} + ry_nz_n + d) = 0$$

$$\sum_n w_n (px_nz_n + qy_nz_n + rz_n^{\,2} + d) = 0$$

$$\sum_n w_n (px_n + qy_n + rz_n + d) = 0$$

These are then solved for the values p, q, r and d required to define the plane.

The angle (ϕ) between the planes $p_1x + q_1y + r_1z + d_1 = 0$ and $p_2q + q_2y + r_2z + d_2 = 0$ is given by:-

$$\phi = \cos^{-1} (p_1p_2 + q_1q_2 + r_1r_2)$$

2.8. Experimental

X-Rays were produced from sealed tubes using copper ($\bar{\lambda}(K_\alpha) = 1.5418$ Å) and molybdenum ($\bar{\lambda}(K_\alpha) = 0.7107$ Å) targets, by means of a 1KW. Solus-Schall and a 750W. Phillips 1008 generator. "Leeds" and

"Unicam" Weissenberg cameras and a Buerger precession camera (with universal-joint suspension) were used to collect single-crystal diffraction data. Intensity photographs were taken using Ilford Industrial G, B and C X-ray films, and were processed using Ilford PQX - 1 developer, an acetic acid hardening bath and Ilford IF-9 fixer.

Single crystals, selected for the investigations after careful examination under a polarizing microscope to check against obvious twinning, were mounted on very thin soda glass fibres using Durofix or Seccotine. Air-unstable and volatile crystals were either coated with a layer of polymer ('polyvinyl formal' from a 2% solution in 1,2-dichloroethane) or sealed in a Lindemann tube. The fibres were mounted on standard crystallographic arcs and the crystals accurately aligned along a simple cyrstallographic axis by examination of a series of setting photographs. The maximum permissible error in alignement was found to be ≈ 15' on the Weissenberg and ≈ 2' on the precession cameras.

Intensity photographs for a given zone were taken with an initial exposure of 64 hrs. and subsequent shorter exposures (down to ≈ $\frac{1}{8}$hr.). The intensities of reflexions were estimated visually by comparison with a calibrated intensity strip (ideally, made from the same crystal) having a series of weak spots of nominal intensity 1→24. Some precession-film intensities were originally measured using a Joyce-Loebl microdensitometer, but this method was discontinued since visual data was found to be the more accurate. All films in a given zone were scaled to the strongest by comparison of measurable reflexions on consequent films.

All calculations were performed on the University of London Ferranti "Mercury" Digital Computer and similar machines belonging to the University of Sheffield and B.P.

I am indebted to the following people for providing copies of their computer programmes: Dr. J. S. Rollett (Structure Factor calculation, with least-squares refinement); Mr. O. S. Mills (Fourier); Dr. R. A. Sparks (distance-angle calculations; molecular axes; molecular vibration elipsoids); Dr. J. A. Bland (data reduction, including Weissenberg L.P.F.); Mrs. J. Dollimore (precession L.P.F.); Mr. N. A. Bailey (scale-sort programme and many miscellaneous data processing programmes).

2.9. Appendix

The symbols a,b,c are used to define the unit-cell axes (in directions x,y,z). The angle between a and b is γ, between b and c is α and between a and c is β. The Miller indices $hk\ell$ are associated with the intercepts on the a,b,c axes respectively.

V is the volume of the unit cell and A the area of a projection down an axis of the unit cell.

The reciprocal lattice parameters are a^*, b^*, c^*, α^*, β^*, γ^*. As with the real-space parameters, the reciprocal lattice constants have both direction and magnitude. a^* is perpendicular to the bc plane and is the reciprocal of the perpendicular distance between successive planes in the 100 stack (i.e. $a^* = d^*_{100} = 1/d_{100}$). b^* and c^* are similarly defined with respect to the ac, ab planes and 010, 001 stacks.

The relationships between real and reciprocal lattice parameters are :-

$$a^* = \frac{bc \sin \alpha}{V}$$

$$b^* = \frac{ac \sin \beta}{V}$$

$$c^* = \frac{ab \sin \gamma}{V}$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}$$

$$\cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma}$$

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos\gamma}{\sin \alpha \sin \beta}$$

The volume of the unit cell is given by:-

$$V = 2\,abc \sqrt{\sin(s) \sin(s-\alpha) \sin(s-\beta) \sin(s-\gamma)}$$

where $2s = \alpha + \beta + \gamma$.

The perpendicular distance, $d_{hk\ell}$, between successive members of a stack of planes $(hk\ell)$ is:-

$$d_{hk\ell} = \left((ha^*)^2 + (kb^*)^2 + (\ell c^*)^2 + 2k\ell b^*c^* \cos \alpha^* + 2h\ell a^*c^* \cos \beta^* + 2hka^*b^* \cos \gamma^* \right)^{-\frac{1}{2}}$$

The Bragg equation, $n\lambda = 2d \sin \theta$, leads to an expression for the Bragg angle:-

$$\sin^2 \theta_{hk\ell} = \frac{\lambda^2}{4} \left((ha^*)^2 + (kb^*)^2 + (\ell c^*)^2 + 2k\ell b^*c^* \cos \alpha^* + 2h\ell a^*c^* \cos \beta^* + 2hka^*b^* \cos \gamma^*\right)$$

C H A P T E R III

THE CRYSTAL AND MOLECULAR STRUCTURE OF π-CYCLOPENTADIENYL-1-PHENYLCYCLOPENTADIENECOBALT

3.1. Metal-cyclopentadiene complexes

The reaction of cobalt chloride with sodium cyclopentadienide in tetrahydrofuran produces the "sandwich" compound bis-π-cyclopentadienylcobalt (Wilkinson, Birmingham and Cotton, 1956), as with other first row transition elements. A similar reaction, using rhodium trichloride, resulted in the isolation of a compound of formula $C_{10}H_{11}Rh$, which was at first (Liehr, 1957) believed to be a hydride. Green, Pratt and Wilkinson (1959) later prepared a series of organometallic compounds in which there was a cyclopentadiene or substituted cyclopentadiene residue, and recognised $C_{10}H_{11}Rh$ as such a compound. Most of this work was, however, with cobalt complexes.

The unsubstituted compound $(\pi\text{-}C_5H_5)\ CoC_5H_6$ was prepared from the cobalticinium ion by hydride reduction:-

$$(\pi\text{-}C_5H_5)_2\ Co^+ \xrightarrow{BH_4^- \text{ or } AlH_4^-} \pi\text{-}C_5H_5CoC_5H_6$$

This compound showed some interesting spectroscopic properties. The infra-red spectrum revealed a very intense, broad, band at 2742 cm^{-1}, which was shown to be due to a fundamental carbon-hydrogen stretching mode by comparison with the spectrum of the compound formed by deuteride ion attack on the cobalticinium ion. The deutero-compound, $\pi\text{-}C_5H_5CoC_5H_5D$, had a corresponding band shifted down to $\simeq$ 2050 $cm.^{-1}$ (giving

$\nu_{C-H}/\nu_{C-D} = 1.34$, which is sufficiently close to the theoretical $\sqrt{2}$ to confirm that the stretch is fundamental). The broad, anomalously low, carbon-hydrogen stretching frequency was attributed to weakening of the C-H_α bond which resulted from some interaction of the endo-hydrogen (H_α) with the cobalt atom. (see Figure 3.1 (I))

The proton magnetic resonance spectrum showed that the compound did indeed retain one π-C_5H_5 residue unchanged, and that the two aliphatic protons in the cyclopentadiene ring were non-equivalent: H_α showed a resonance at $\tau = 8.05$ (shown by comparison with the deutro-compound), and the other proton, termed H_β , at the saturated carbon, had a resonance at $\tau = 7.32$. The shift of H_α to high field relative to H_β was in keeping with the "partially hydridic" nature of this atom due to its interaction with the cobalt. The remaining four protons of the cyclopentadiene appeared as complex multiplets at $\tau = 4.80$ (H_{3+4}) and $\tau = 7.55$ (H_{2+5}). This difference in resonance position was attributed to the non-uniform shielding effects of the cobalt atom and the cyclopentadiene was assumed to bond to the cobalt atom via two π-bonds.

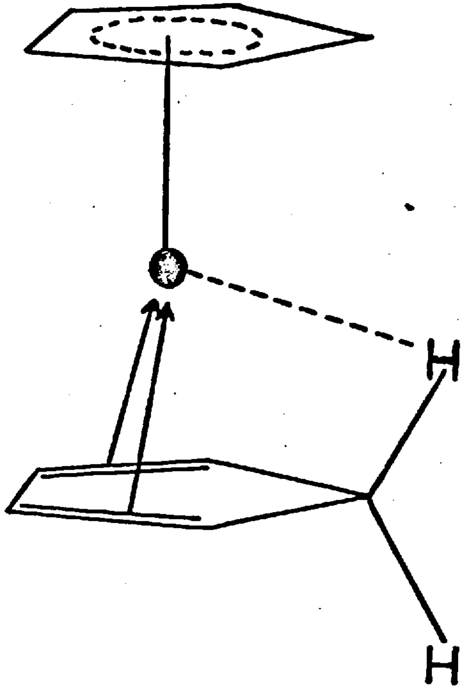
Substituted cyclopentadiene complexes have been made by two routes:-

(i) From an organic halide and cobaltocene (Green, Pratt and Wilkinson, 1959) :-

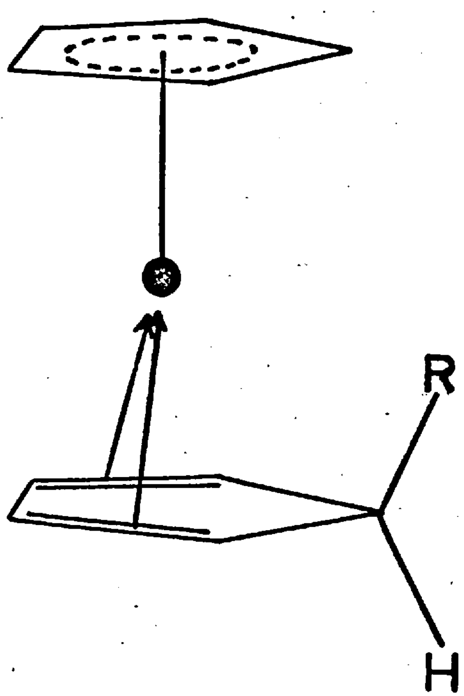
$$(\pi\text{-}C_5H_5)_2\,Co + R\text{-}X \rightarrow (\pi\text{-}C_5H_5)\,CoC_5H_5R + (\pi\text{-}C_5H_5)_2\,Co^+X^-.$$

where R-X = $C\ell_3C$-$C\ell$, CH_3-I, CF_3-I, $C\ell_2CH$-$C\ell$ etc.

Figure 3.1



I



II

(ii) From an alkyl- or aryl-lithium complex and a cobalticinium salt (Fischer and Herberich, 1961):-

$(\pi\text{-}C_5H_5)_2\ Co^+X^- \ + \ LiR \rightarrow (\pi\text{-}C_5H_5)\ CoC_5H_5R \ + \ LiX$

$X^- = I^-,\ C\ell^-,\ C\ell O_4^-$ etc.; $R = CH_3\text{-},\ C_6H_5\text{-}$ etc.

Since none of the substituted complexes, $(\pi\text{-}C_5H_5)\ Co\ (C_5H_5R)$, showed the anomalously low $C\text{-}H_\alpha$ stretching frequency in the infra-red or the H_α resonance in their p.m.r spectra, they were formulated as the endo- isomers, i.e. with R taking the stereochemical position of H_α (see Figure 3.1 (II))

No complete X-ray analysis of metal-cyclopentadiene compounds had been reported although Starovskii and Struchkov (1961) made a preliminary investigation of $Co_2(C_5H_5)_5$ which appeared to be completely inconsistent with the later suggestion (Fritz and Keller, 1962) that this compound was, in fact, $(\pi\text{-}C_5H_5CoC_5H_5\text{-})_2C_5H_4$.

The present study was thus undertaken with the object of determining:-

(i) the nature of the metal-cyclopentadiene bonding, and

(ii) the conformation of the substituent R (in this case, $R = C_6H_5$).

3.2. Experimental

π-Cyclopentadienyl-1-phenylcyclopentadienecobalt $(\pi\text{-}C_5H_5.Co.C_5H_5.C_6H_5)$ was prepared by the reaction of lithium phenyl with bis-π-cyclopentadienylcobalt iodide $((\pi\text{-}C_5H_5)_2\ Co^+I^-)$ and recrystallised by slow evaporation of a solution in petroleum ether (b.p. 40 - 60°C). The deep-red air-stable crystals were orthorhombic with well developed (100) and (010) faces. An essentially cube-shaped crystal of side 0.2 mm. was selected for the X-ray crystallographic analysis.

Molybdenum K_α radiation ($\bar{\lambda}$ = 0.7107) was filtered (zirconium filter) for collecting precession data from the $h0\ell$, $h1\ell$ and $h2\ell$ zones. Equi-inclination Weissenberg photographs of the hk0, hk1, hk2, hk3 and hk4 zones, taken with unfiltered molybdenum radiation, were used to complete the data. Ilford Industrial G, B and C films were found to give a satisfactory range of intensities for use in a tri-pack for Weissenberg photographs, but single G films were used in collecting the precession data. Relative intensities of the precession data were estimated by the use of a Joyce-Loebl microdensitometer; the Weissenberg data, together with the very weak reflexions of the precession photographs were measured visually.

3.3. Unit Cell and Spacegroup.

Unit-cell dimensions were determined by a least-squares analysis of high-angle precession data, giving the values:-

$$a = 29.64 \pm 0.04\ \text{Å}$$

$$b = 7.70 \pm 0.01\ \text{Å}$$

$$c = 10.68 \pm 0.02\ \text{Å}$$

Since the crystal is orthorhombic, the volume of the unit cell is given by V = abc. Hence:-

$$V = 2493\ \text{Å}^3$$

The observed density, measured by flotation in Rohrbach's solution (methanolic BaI_2 and HgI_2) is $\rho_{obs} = 1.44 \pm 0.01$ gm. cm.$^{-3}$ This agrees with the calculated value, $\rho_{calc.} = 1.449$ gm. cm.$^{-3}$ for a compound of molecular weight 266 and eight molecules per unit cell.

The only systematic absences observed were $0k\ell$ for $k = 2n + 1$, $h0\ell$ for $\ell = 2n + 1$, and $hk0$ for $h = 2n + 1$. Since $Z = 8$, this leads to the unique assignement of the spacegroup as Pbca (D_{2h}^{15}, No. 61) with molecules in general positions.

3.4. Solution of the Phase Problem

The equipoints for spacegroup Pbca are:-

$\pm$ (x, y, z)

$\pm$ (x, $\frac{1}{2}$ - y, $\frac{1}{2}$ + z)

$\pm$ ($\frac{1}{2}$ + x, $\frac{1}{2}$ - y, - z)

$\pm$ ($\frac{1}{2}$ + x, y, $\frac{1}{2}$ - z)

The unit cell contains eight units of $CoC_{16}H_{15}$. Consequently, the total number of interatomic vectors in one Patterson unit cell is vast (the number of vectors is given by $n^2 - n$, when n is the number of atoms per unit cell; hence $n^2 - n = (8 \times 32)^2 - (8 \times 32) = 65280$). However, when using the "heavy atom" technique for phase solution, it is legitimate to assume that the highest peaks on the Patterson map are most likely to be due to heavy atom - heavy atom vectors.

So, the above equipoints can now be taken as the cobalt positions in the unit cell. By taking the equipoints one pair at a time, and subtracting, to obtain the vector between them, we arrive at the following 56 ($n^2 - n = 56$, for $n = 8$) vectors (the symbol m stands for the multilplicity of the peak).

m = 4 :	0,	$\frac{1}{2} + 2y$,	$\frac{1}{2}$
	0,	$\frac{1}{2} - 2y$,	$\frac{1}{2}$
	$\frac{1}{2}$,	0,	$\frac{1}{2} + 2z$
	$\frac{1}{2}$,	0,	$\frac{1}{2} - 2z$
	$\frac{1}{2} + 2x$,	$\frac{1}{2}$,	0
	$\frac{1}{2} - 2x$,	$\frac{1}{2}$,	0
m = 2 :	$\frac{1}{2}$,	$\frac{1}{2} + 2y$,	$2z$
	$\frac{1}{2}$,	$\frac{1}{2} + 2y$,	$-2z$
	$\frac{1}{2}$,	$\frac{1}{2} - 2y$,	$2z$
	$\frac{1}{2}$,	$\frac{1}{2} - 2y$,	$-2z$
	$2x$,	$\frac{1}{2}$,	$\frac{1}{2} + 2z$
	$2x$,	$\frac{1}{2}$,	$\frac{1}{2} - 2z$
	$-2x$,	$\frac{1}{2}$,	$\frac{1}{2} + 2z$
	$-2x$,	$\frac{1}{2}$,	$\frac{1}{2} - 2z$
	$\frac{1}{2} + 2x$,	$2y$,	$\frac{1}{2}$
	$\frac{1}{2} - 2x$,	$2y$,	$\frac{1}{2}$
	$\frac{1}{2} + 2x$,	$-2y$,	$\frac{1}{2}$
	$\frac{1}{2} - 2x$,	$-2y$,	$\frac{1}{2}$
m = 1 :	$2x$,	$2y$,	$2z$
	$2x$,	$2y$,	$-2z$
	$2x$,	$-2y$,	$2z$
	$2x$,	$-2y$,	$-2z$
	$-2x$,	$2y$,	$2z$
	$-2x$,	$2y$,	$-2z$
	$-2x$,	$-2y$,	$2z$
	$-2x$,	$-2y$,	$-2z$

A two-dimensional Patterson projection is independent of the coordinate down the axis of projection. Thus, projecting down b increases the multiplicities, and lowers the number, of observed peaks. The vectors, and multiplicities, for a projection down b are:-

$m = 8$:	0,	$\frac{1}{2}$
$m = 4$:	$\frac{1}{2}$,	$\frac{1}{2} + 2z$
	$\frac{1}{2}$,	$\frac{1}{2} - 2z$
	$\frac{1}{2}$,	$2z$
	$\frac{1}{2}$,	$- 2z$
	$\frac{1}{2} + 2x$,	0
	$\frac{1}{2} - 2x$,	0
	$\frac{1}{2} + 2x$,	$\frac{1}{2}$
	$\frac{1}{2} - 2x$,	$\frac{1}{2}$
$m = 2$:	$2x$,	$2z$
	$2x$,	$- 2z$
	$- 2x$,	$2z$
	$- 2x$,	$- 2z$
	$2x$,	$\frac{1}{2} + 2z$
	$2x$,	$\frac{1}{2} - 2z$
	$- 2x$,	$\frac{1}{2} + 2z$
	$- 2x$,	$\frac{1}{2} - 2z$

A Patterson synthesis P(UoW) using the 190 reflexions of the $h0\ell$ zone as Fourier coefficients, showed a set of vector peaks consistent, both in position and multiplicity with cobalt coordinates $x = 0.083$ and $z = 0.139$. The synthesis P(UVo) showed a series of vector peaks from which the third coordinate of the cobalt, $y = 0.010$, was easily determined;

no three-dimensional Patterson was therefore required.

3.5. Determination of the Structure

(i) Development of the projection on 010.

The electron density synthesis $\rho(x0z)$, phased by the cobalt contribution only, had a reliability index R (defined as $R = \sum (F_{obs} - F_{calc}) / \sum F\ calc$) of 0.56. This reduced to R = 0.33 after a single cycle of least-squares refinement. The first $\rho(x0z)$ synthesis showed a clearly resolved phenyl carbon atom (C6) of the cyclopentadiene ligand to which the phenyl group is directly attached. A second electron density synthesis, phased by the cobalt and seven carbon atoms, showed a further three peaks which could be assigned to carbon atoms of the π-cyclopentadienyl ligand; a final Fourier synthesis allowed a further three atoms to be located. Severe overlap (see Figure 3.2 for $\rho(x0z)$ at this stage) prevented the further development of the 010 projection. A subsequent difference Fourier was of little help in positioning the remaining atoms, which were finally given atomic coordinates consistent with bond-length and bond-angle considerations. The reliability factor then reduced from 0.25 to 0.16 in three cycles of least-squares refinement (a comparison with the correct structure later showed that two atoms had been incorrectly positioned by this procedure).

(ii) Development of the projection on 001.

The 95 reflexions of the hk0 zone, phased by the cobalt atom, gave a reliability index of 0.55 which reduced to 0.47 after one cycle of least-squares refinement. The electron-density synthesis down c showed the approximate positions of the six carbon atoms of the phenyl group, but immediately indicated the need for a three-dimensional analysis because of atomic overlap on, and around, the mirror planes at $y = \pm \frac{1}{4}$. The cyclopentadienyl group was near the mirror-plane at $y = \frac{1}{4}$, and the cyclopentadiene around $y = -\frac{1}{4}$ (see Figure 3.3) . Since C6 is almost at $y = -\frac{1}{4}$, two suitable positions for the phenyl ring, mirrored about $y = -\frac{1}{4}$, are possible.

(iii) Three-dimensional analysis.

The spectroscopic evidence, suggesting that the phenyl group occupies the endo-position, was therefore used to select one of the alternative sets of y-coordinates for the phenyl group, and the first three-dimensional Fourier synthesis was calculated on the basis of the cobalt and the six carbon atoms of the (endo-) phenyl group-contributions to the structure factors. The reliability index was then 0.36 and the carbon atoms of the endo-phenyl group, which had been used in the phasing, appeared only as weak peaks. Quite strong "ghost" peaks appeared in the exo-position, and a second three-dimensional analysis, selecting the exo-possibility for the

Figure 3.2 h0l Fourier

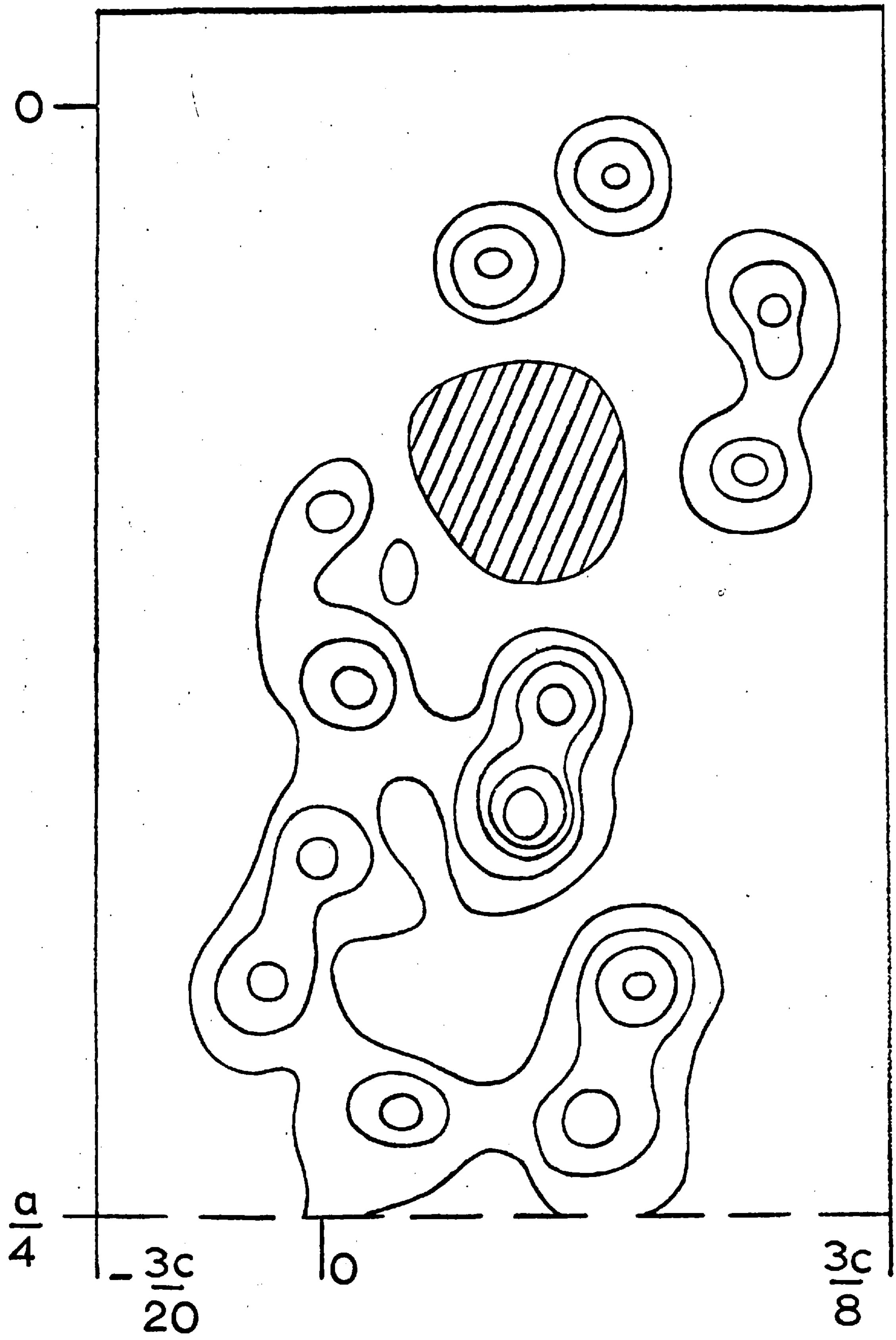
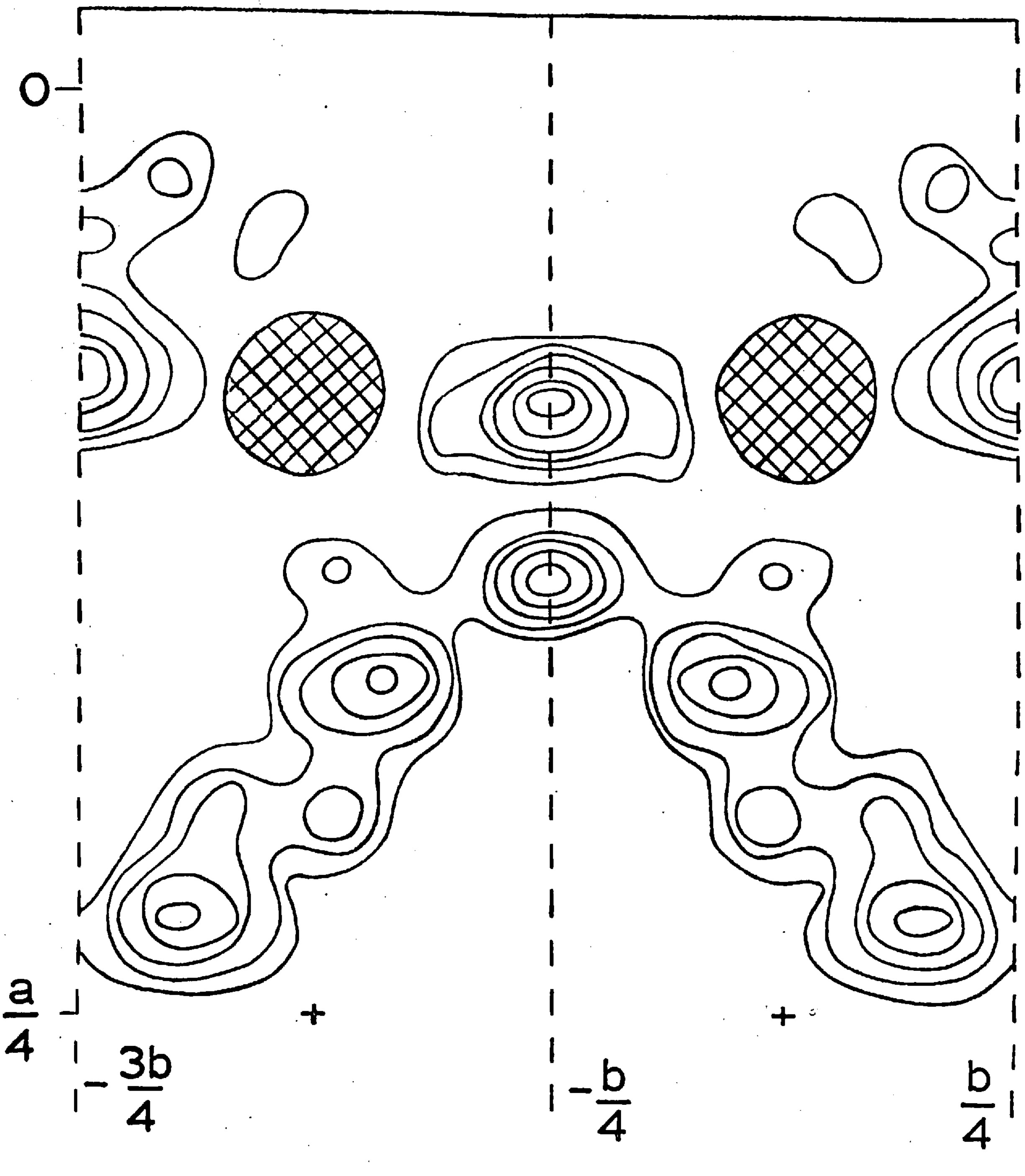


Figure 3.3 hk0 Fourier



phenyl-carbon atoms (i.e. substituting x, $\frac{1}{2}$ - y, z for the previous x, y, z) showed peaks corresponding to all the remaining carbon atoms.

The structure factors, based now on phasing from the cobalt and all sixteen carbon atoms, gave $R_{hk\ell}$ as 0.214. Two cycles of positional parameter refinement, together with isotropic carbon and anisotropic cobalt temperature factor refinement, reduced this value to 0.163. Refinement of anisotropic Debye factors and positions of all atoms reduced $R_{hk\ell}$ to 0.089 in six cycles of least-squares refinement, at which point further significant refinement was impossible. The 815 observed structure factors (see Table 3.1) were refined using a unit weighting scheme; the $F_{calc.}$ values do not contain any contribution from the fifteen hydrogen atoms present.

The maximum coordinate shift indicated by the last cycle of least-squares refinement was less than 0.003 Å (i.e. less than one-sixth of the average atomic standard deviation). The final atomic coordinates listed in Table 3.2., and final anisotropic thermal parameters in Table 3.3., each with its estimated standard deviation (e.s.d.).

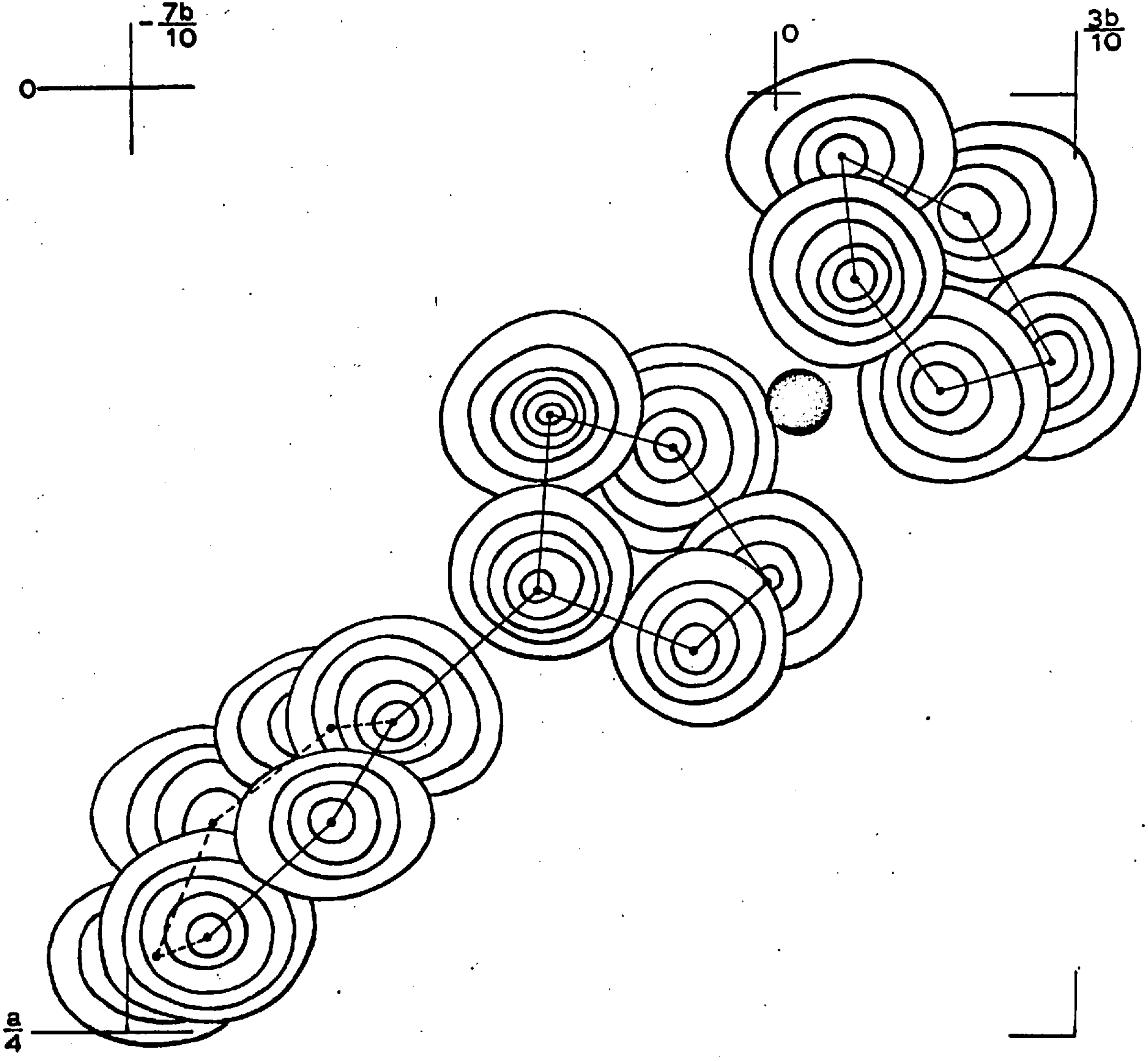
3.6. The Molecular Structure

The composite electron density synthesis is shown in Figure 3.4. Intramolecular bond lengths and bond angles, with their standard deviations are collected in Table 3.4. The essential geometry of the molecule, together with the numbering of the atoms, is shown in Figure 3.5.

Detailed examination of the intramolecular bond lengths shows that the "diene" should be regarded as a six-electron donor to a d^6 cobalt atom in a formal + 3 oxidation state, rather than a four-electron donor to a d^8 (+ 1) cobalt ion, as previously believed. Two electrons are donated to form σ-bonds at each of the carbon atoms C7 and C10, and the proximity of C8 and C9 to the cobalt indicates that a further two electrons must be involved in forming a metal-ligand π-bond from the cobalt to the centre of the C8 - C9 bond. This unexpected result is clearly demonstrated by:-

(i) the considerable non-planarity of the cyclopentadiene ligand. Carbon atoms C7, C8, C9 and C10 are strictly planar, the direction cosines to the normal of this plane being -0.5764, 0.7161, 0.3938 (referred to the orthogonal crystal axes a,b and c) and the root mean square deviation of the four atoms from this plane is 0.005 Å. The normal to the plane containing the three atoms C6, C7 and C10 has direction cosines -0.3902, 0.3387, 0.8562. These two planes in the cyclopentadiene ring are thus tilted at an angle of 36.5° with respect to one another. This new ring conformation can be explained only by a change in hybridization of the atoms C7 and C10 from an sp^2 valence state in the uncoordinated ligand to an sp^3 state in the present complex, in which the fourth bonds of the (distorted) tetrahedra at C7 and C10 are directed towards the cobalt, forming two localized carbon-metal σ-bonds.

Figure 3.4
Composite Electron Density Synthesis.



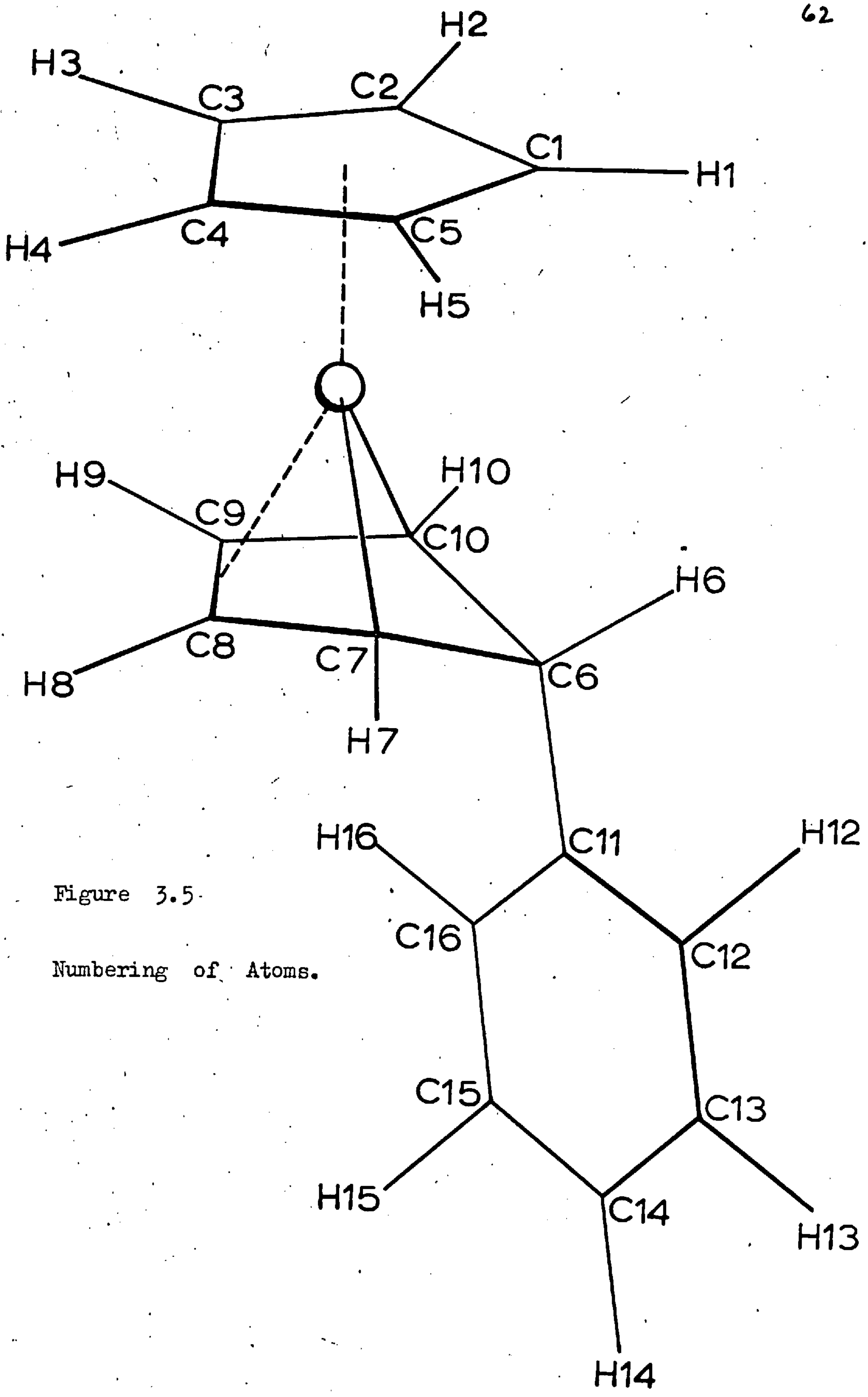


Figure 3.5

Numbering of Atoms.

(ii) the detailed bond-lengths in the cyclopentadiene ring (see Figure 3.6) show that only one short bond, C8 - C9 (of length 1.36 ± 0.03 Å) is present, and that this is directly opposite C6, the saturated atom of the cyclopentadiene ligand. The remaining average bond-lengths in the ring are 1.51 Å (for C7 - C8 and C9 - C10) and 1.52 Å (for C6 - C7 and C6 - C10); these two values are within standard deviations of the values expected, since the sum of the covalent carbon radii $r_{sp^2} + r_{sp^3}$ is 1.51 Å while $r_{sp^3} + r_{sp^3}$ is 1.54 Å.

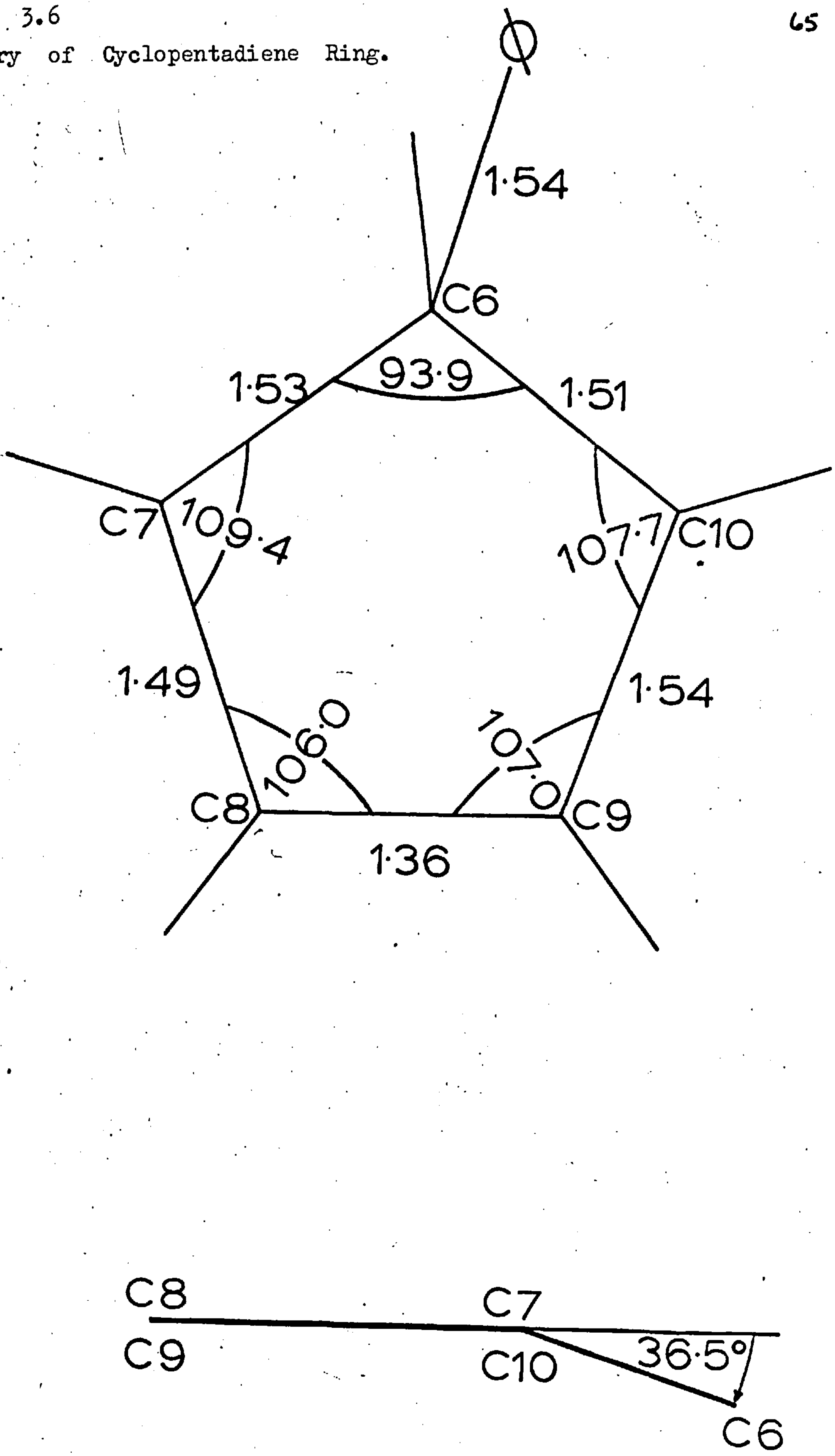
(iii) the anomalously low value of $93.9 \pm 1.5^{\circ}$ for the angle C10 - C6 - C7 suggests that localized bonding from the carbon atoms C7 and C10 results in these two atoms being squeezed closer together in order to form larger overlap integrals between the localized carbon sp^3 orbitals at these centres and the metal d orbitals than is possible for carbon atoms arranged in a regular pentagon.

The σ-bonding carbon atoms, C7 and C10, are arranged so that the mean cobalt-carbon distance is 2.00 ± 0.02 Å, which is also the mean distance of C8 and C9 from the cobalt ion. The distance from the metal to the centre of the C8 - C9 bond is considerably less than this value, demonstrating $d_{\pi} - p_{\pi}$ bonding (of the type termed μ-bonding by Pauson, 1960). Chemically, the cobalt ion must be regarded as a good dienophile, since the cyclopentadiene residue has effectively undergone 1,4-Diels-Alder addition.

The present structure determination provides some explanation for a number of the observed properties of substituted cyclopentadiene complexes of cobalt (Green, Pratt, Wilkinson, 1950). The high resolution proton magnetic spectrum of π-cyclopentadienyl-1-phenylcyclopentadienecobalt shows that the protons H7 and H10 are equivalent, as are H8 and H9 of the diene system. These two sets of protons each occur as doublets, centred at $\tau = 7.19$ and $\tau = 4.86$ respectively (Jones and Wilkinson, 1963). Since in the uncoordinated cyclopentadiene molecule the four diene protons appear at a single resonance position (Stohmeier, Lombardi and Lemmon,1959), it was originally assumed that the non-equivalence of the protons in the metal complex arose from anomalous magnetic shielding effects produced by the cobalt ion. The conformation of the diene (Figure 3.6.) suggests that, in the light of the present studies, the large chemical shift between the two resonance frequencies can be more simply interpreted in terms of hybridization differences at the respective carbon atoms, the low-field resonance being typical of protons bound to olefinic carbon atoms and that at the higher field being associated with the essentially sp^3 hydridized carbon atoms, C7 and C10.

In simple valence-bond terms, the cobalt ion in π-cyclopentadienyl-1-phenylcyclopentadienecobalt can be regarded as essentially octahedrally coordinated (with, of course, a large trigonal distortion), the configuration being made up by three bonds (2σ-' s and 1 π) from the cyclopentadiene ligand, together with three bonds to points in the π-cyclopentadienyl ring. (This description of a π-cyclopentadienyl ligand as a formal tridentate ligand (Fischer and Pfab, 1952) is used for its qualitative stereochemical usefulness, rather than its fundamental validity).

Figure 3.6
Geometry of Cyclopentadiene Ring.



The diamagnetism of the complex reflects the pseudo-inert gas configuration of the metal, the eighteen-electron structure being built up through the six-electron donation from each of π-cyclopentadienyl and cyclopentadiene ligands to the d^6 cobalt (+ 3) ion. The diamagnetism is no criterion of structure, since an eighteen-electron structure would still be obtained in Figure 3.1, the cyclopentadiene ligand now contributing only four electrons to the d^8 cobalt (+ 1) ion, which becomes effectively five-coordinate.

The π-bonded cyclopentadienyl ring is planar (r.m.s. deviation, 0.030 Å), the direction cosines to the normal being -0.5764, 0.6707, 0.4680. The Co - C3 bond length of 2.15 Å appears to be significantly greater than the remaining Co - C distances ($\bar{x} = 2.06$ Å) although the reason for this is not easy to understand, at least on the basis of intramolecular bonding. The cobalt-centre of π-cyclopentadienyl ring distance is 1.67 Å compared with a value of 1.59 Å for the cobalt-centre of gravity of the carbon atoms C7, C8, C9 and C10. The cyclopentadiene and π-cyclopentadienyl rings are in the eclipsed configuration, the respective planes being 5.1° from parallel; the slight departure from parallelness may be due to intermolecular interactions (vide infra). The average carbon-carbon bondlength of 1.46 Å in the cyclopentadienyl ring is somewhat larger than might have been expected, but the e.s.d. of 0.03 Å (and the fact that hydrogen atom contributions to the structure factors have been ignored) precludes any quantitative discussion of the possible significance of this result.

The phenyl group occupies the exo- position and has essential D_{6h} symmetry; the average carbon-carbon bond-length is 1.41 ± 0.02 Å, the r.m.s. deviation of the six atoms from a plane having direction cosines to the normal -0.6877, -0.6899, 0.2262 being 0.03 Å. The plane containing the carbon atoms C7, C6 and C10 is at an angle of 80.3° to that of the phenyl ring. (It is interesting to note that were this angle exactly 90°, the molecule could possess a mirror plane containing the cobalt atom and phenyl group, and bisecting the two five-membered rings: however, see Section 3.7.) .

The coordinates of the fifteen hydrogen atoms have been calculated assuming normal valence angles and a uniform carbon-hydrogen bond-length of 1.08 Å (see Table 3.5.) . A final difference synthesis, based on the cobalt and carbon contributions only to the F_{calc}'s, shows that (with the exception of H4) each of the calculated hydrogen positions occurs at a residual peak of electron density varying from 0.3 to 0.5 e. $Å^{-3}$ in height. It must be emphasised that these peaks are rather diffuse and would not lead to the accurate determination of the hydrogen atom coordinates by difference Fourier techniques alone.

The angle of tilt of the cyclopentadiene ligand is so great that C6 is 2.56 Å from the metal (as opposed to an average of 2.00 for C7 → C10). The hydrogen atom H6, attached to C6, although in a formal endo- configuration, is situated at a distance of 3.05 Å from the metal. This distance is too great to allow any appreciable cobalt-hydrogen interaction and, indeed, it can be shown by simple geometric calculations, that only when the cyclopentadiene approaches planarity can this phenomenon occur.

3.7. The Crystal Structure

The arrangement of molecules in the crystal as viewed along the b- axis is shown in Figure 3.7. The packing down c (Figure 3.8.) is particularly interesting since it shows that the dove-tailing of the phenyl groups is one of the dominant features in the "choice" by the molecules of Pbca as the preferred spacegroup. A list of the closest molecular contacts is collected in Table 3.6. A significant feature of these molecular contacts is the sandwiching of H12 by an intramolecular contact to H6 of 2.18 Å and an intermolecular contact (also of 2.18 Å) to H8 $(-x, -\frac{1}{2}-y, \frac{1}{2}+z)$. This distance is shorter than that normally accepted for the van der Waals diameter for hydrogen of ca. 2.50 Å (Pauling, 1960) but there is growing evidence (Coulson and Haigh, 1963; Bailey and Mason, 1963) that the true value is considerably less than 2.50 Å, or at least, that the hydrogen atom is relatively "soft" as regards close contact.

It seems clear that the phenyl group is not orthogonal to the plane formed by C7, C8 and C10 simply due to these interactions. Orthogonality would imply a considerable build-up of the van der Waals repulsive energies. The barrier to free rotation of the phenyl group would thus appear to be reasonably high, and this is consistent with the observation (Jones and Wilkinson, 1961) that the high-resolution nuclear magnetic resonance spectrum of these protons shows a very

Figure 3.7

Packing Diagram - Projection on (010).

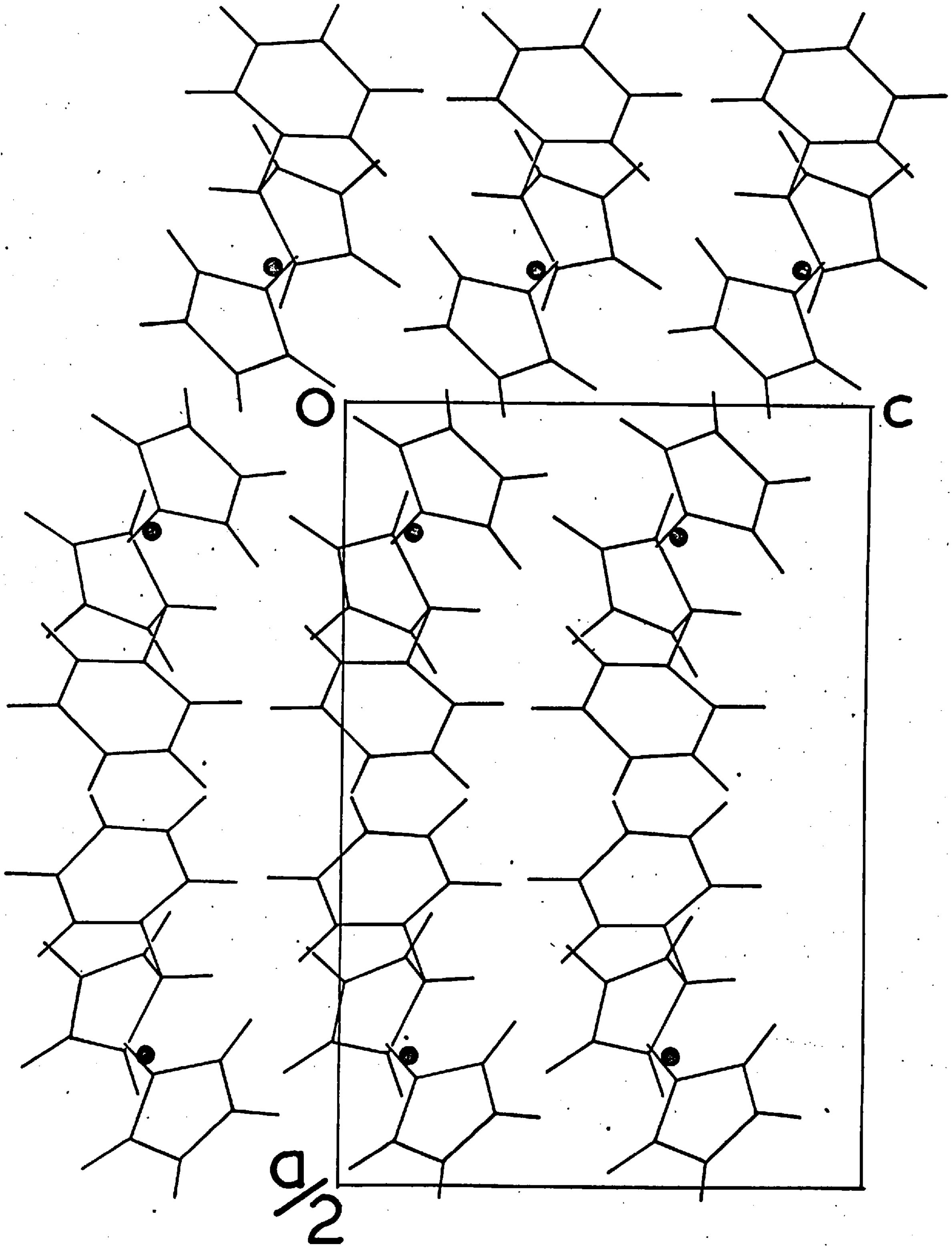
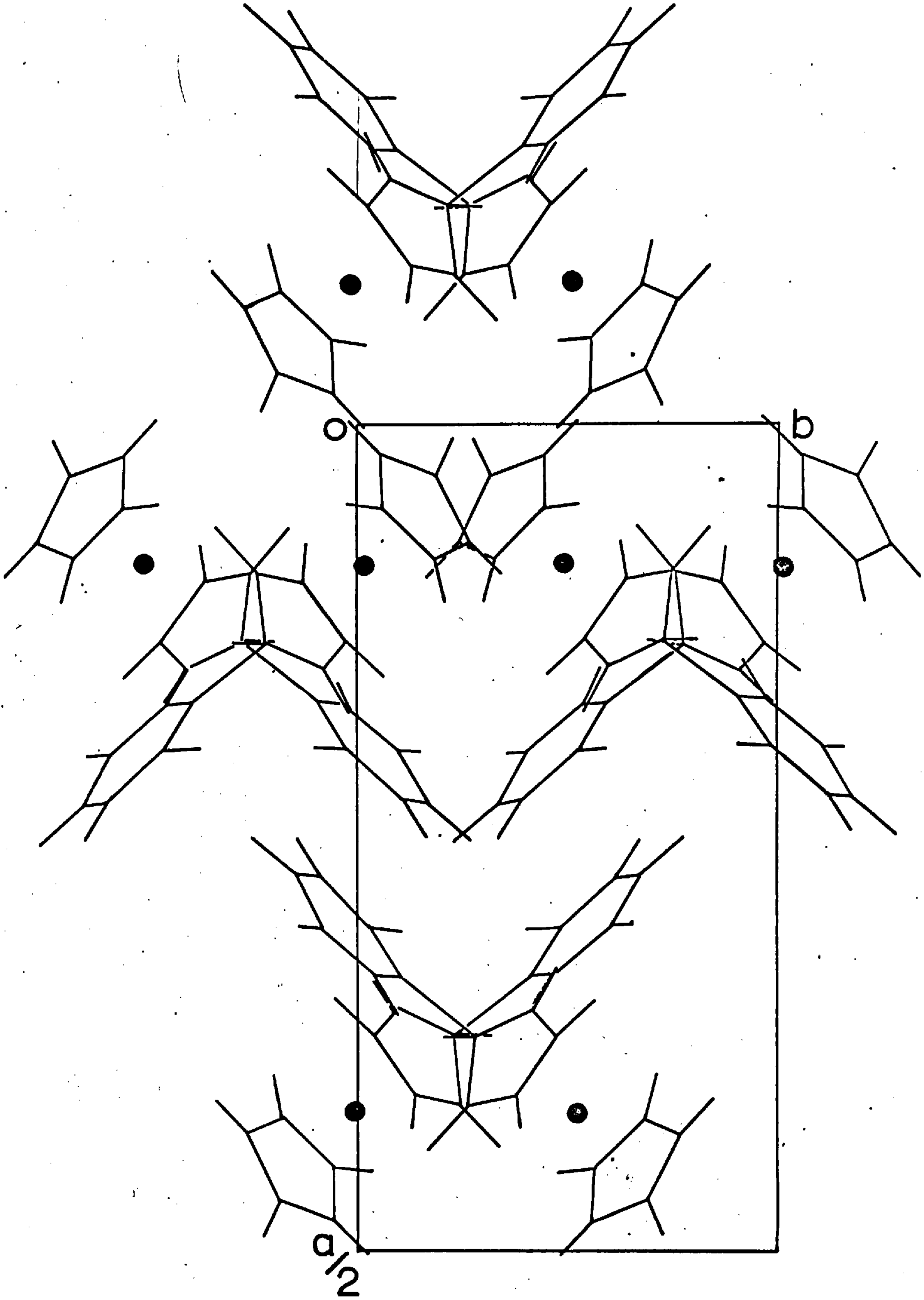


Figure 3.8

Packing Diagram - Projection on (001).



complex fine structure centred at $\tau = 3.2$.

Root mean square amplitudes and direction cosines of the major, median and minor axes of the atomic vibration ellipsoids are given in Table 3.7. The major axis of the vibration ellipsoid of the cobalt is orientated at an angle of 68° to the normal in the plane of the π-cyclopentadienyl ring, the minor axis making an angle of only 27° to this direction. As is to be expected, the cobalt atom is vibrating almost isotropically in the space between the two eclipsed rings, with a much smaller motion in direction towards the ring. The large e.s.d.'s of the Debye factors of the carbon atoms make any breakdown of the $\overline{u^2}$ into rigid body vibrational modes a somewhat tenuous procedure. Large librational motions about the five-fold axis of the cyclopentadienyl ring seem quite clear.

3.8. The Attempted X-Ray Structural Analysis of π-cyclopentadienylcyclopentadienecobalt.

The completed crystal structure analysis of π-cyclopentadienyl-1-phenylcyclopentadienecobalt explained some of the anomalies observed i.e. the proton magnetic resonance spectrum and the high thermal and aerobic stability of the compound. (As originally formulated, the Co(+ 1) would be expected to be air-sensitive). However, one thing left entirely unexplained was the origin of the anomalously low carbon-hydrogen stretching frequency at 2742 cm.$^{-1}$ in the parent compound $(\pi\text{-}C_5H_5)CoC_5H_6$.

A number of attempts were made to examine single crystals of π-cyclopentadienyl-cyclopentadienecobalt which, being extremely air-sensitive, were mounted on glass fibres in sealed Lindemann tubes of borate glass. In every case, the crystal was seen to slowly melt (over the course of half an hour) in the X-ray beam, probably due to some self-polymerisation reaction in the crystal.

The only crystallographic information obtained was that the crystals were monoclinic with $b \leqslant 6.0$ Å. Consequently the origin of the $C - H_\alpha$ stretch is, as yet, unconfirmed.

TABLE 3.1.

Observed and Calculated Structure Factors for π-C_5H_5 Co C_5H_5 C_6H_5

pp. 74-74a.

Planes are arranged in blocks of constant h and k; the three columns give ℓ, $|F_{obs}|$, $F_{calc.}$

0	0	
0		821.0
2	35.8	-27.7
4	133.4	-135.8
6	121.1	130.4
8	90.7	80.5
10	33.8	-31.0
12	74.9	-70.0
14	28.8	28.9
0	2	
0	188.3	209.7
1	72.8	-71.1
2	10.9	-6.7
4	38.7	-44.8
6	73.4	76.3
8	54.2	61.6
10	29.9	-28.6
12	55.4	-40.6
0	4	
0	180.3	180.5
1	50.6	-35.0
2	47.2	-44.0
4	89.3	-88.9
0	6	
0	44.7	38.3
2	37.8	-35.6
4	35.6	-27.9
0	8	
0	44.7	39.8
2	15.7	-18.5
4	37.8	-37.8
1	0	
2	259.8	-276.4
4	73.4	77.6
6	74.8	77.8
8	33.8	-25.8
10	19.5	-17.6
12	81.7	85.4
1	1	
1		132.5
2		3.5
3	103.6	-98.4
5	47.7	-58.7
7	99.6	96.5
11	38.8	-43.8
1	2	
1	78.8	71.8
2	57.9	-59.0
3	28.3	21.9
4	44.3	41.9
5	38.8	58.5
6	39.9	38.6
10	87.9	-88.5
1	3	
1	73.6	69.3
3	133.8	-113.4
1	4	
1	8.9	-12.7
2	60.9	-62.0
4	22.9	17.3
1	5	
1	56.5	52.8
3	52.2	-52.6
1	6	
2	15.5	-16.9
4	20.9	-9.0
1	7	
1	28.2	26.8
2	29.0	-27.8
3	35.0	-35.4
1	8	
2	23.2	-23.4
2	0	
0		100.8
2	95.9	-100.6
4	117.9	-105.3
6	13.9	14.8
8	44.7	39.7
2	1	
1	48.9	50.4
3	87.7	-81.9
5	200.8	202.2
9	84.4	-63.5
13	47.4	29.0
2	2	
2	81.7	-77.0
4	49.5	-49.6
6	27.8	28.4
8	33.7	31.5
10	25.9	-22.6
4	3	
0	14.3	23.8
1	93.7	-90.9
2	24.3	22.2
3	78.8	-77.1
4	85.2	48.9
2	4	
0	95.3	97.3
1	8.9	-13.8
3	27.5	23.7
4	66.8	-67.8
2	5	
0	10.3	11.8
2	37.3	-36.9
3	33.0	-37.6
2	6	
0	29.8	30.7
4	32.0	-28.3
2	7	
0	23.5	-26.4
1	26.8	-30.2
3	19.9	-27.0
4	40.8	35.2
2	8	
0	14.0	14.5
3	0	
2	211.6	-230.1
4	92.9	17.1
6	155.9	186.2
8	70.8	-64.7
10	41.0	-41.5
12	74.6	47.5
3	1	
1	74.0	70.8
2	65.3	-94.3
3	21.0	-18.9
5	25.9	27.4
8	23.3	12.4
3	2	
1	22.6	-22.7
2	82.4	-82.8
3	41.5	37.4
5	18.4	14.0
6	47.6	38.4
8	48.2	-40.8
10	42.4	-44.8
12	32.4	17.8
3	3	
1	46.8	-44.1
2	20.0	-21.7
4	27.7	-21.1
3	4	
0	136.3	-133.8
1	24.0	67.6
2	35.8	38.0
3	5	
2	21.7	-41.1
3	6	
2	28.4	-39.3
4	22.0	20.2
3	8	
2	40.2	-39.8
4	0	
0	171.0	-176.3
2	61.1	-55.7
4	75.2	69.0
6	63.8	-66.5
8	83.1	-78.6
10	29.8	21.8
4	1	
1	278.0	-245.0
2	100.6	99.6
3	19.7	-21.4
4	37.6	36.4
5	218.1	120.0
7	22.9	28.5
9	41.4	-30.8
13	30.6	11.4
4	2	
0	62.8	-63.6
2	5.6	5.3
4	48.0	47.4
6	83.9	-83.6
8	47.7	-52.5
10	43.3	19.4
4	3	
0	34.0	-37.4
1	96.8	-92.9
2	13.5	17.9
3	31.8	-31.5
4	55.4	30.7
4	4	
0	91.0	-93.9
1	10.5	-10.9
3	13.3	17.3
4	5	
0	64.0	-62.4
1	57.1	-61.9
3	37.2	-34.4
4	6	
0	18.3	-10.4
4	21.9	8.5
4	7	
0	20.0	-31.4
1	27.6	-32.4
3	43.5	-33.0
4	8	
0	31.4	-28.0
5	0	
2	87.7	-79.5
4	23.9	-18.7
6	49.5	49.2
8	25.5	-24.3
10	20.5	-13.5
5	1	
1	245.2	-233.1
3	45.7	-49.0
5	84.0	64.9
7	97.0	-74.3
11	83.9	45.5
5	2	
1	33.8	28.7
2	13.7	-22.7
4	38.4	40.2
5	29.2	46.4
6	35.4	20.0
7	47.7	-10.2
8	28.8	-23.8
10	17.7	-11.0
5	3	
1	74.0	-71.6
4	48.9	47.8
5	200.9	115.1
8	33.4	30.2
5	4	
2	60.5	-61.1
4	21.9	14.7
5	5	
1	25.5	-27.1
2	21.7	19.4
3	49.7	47.9
5	6	
0	45.5	-42.8
4	10.9	9.4
5	7	
1	18.8	-19.7
2	21.7	17.2
3	41.0	41.9
5	8	
2	21.7	-24.7
6	0	
0	124.0	-120.4
2	52.1	47.0
4	125.7	127.3
6	44.7	-47.3
8	51.7	-40.2
10	30.2	51.6
16	19.0	13.7
24	21.3	-25.5
6	1	
0	160.0	-195.3
4	28.6	24.4
6	25.9	-24.7
6	2	
0	3.0	-13.6
1	48.1	-19.2
3	14.3	-10.0
4	128.2	131.0
6	40.8	-41.7
8	44.2	-23.7
10	44.7	27.3
6	3	
0	40.4	-37.6
1	5.6	6.6
2	21.7	-28.9
4	45.2	-25.9
6	4	
0	104.8	-108.2
2	27.8	31.2
3	40.2	44.7
4	152.1	124.7
6	5	
0	22.5	-21.9
1	3.6	-7.8
6	6	
0	64.6	-66.1
1	24.7	15.1
2	13.3	9.0
3	17.3	15.7
4	51.9	50.4
6	7	
0	10.2	8.4
6	8	
0	28.4	-37.1
7	0	
2	30.4	64.7
4	18.1	-21.5
6	25.5	-23.8
8	48.7	44.0
10	18.3	-13.5
7	1	
1	28.1	-24.4
2	58.3	53.5
3	61.4	61.4
4	29.4	-22.8
5	83.7	79.0
6	47.4	-18.9
7	96.2	-95.7
8	32.0	52.0
11	40.0	59.8
7	2	
1	68.0	-57.3
2	54.2	49.8
3	8.9	-5.1
4	13.3	-21.1
6	41.2	-44.5
8	24.3	27.7
10	20.7	13.3
7	3	
2	85.7	-77.3
4	27.8	22.2
5	94.7	93.7
4	21.9	20.2
7	4	
2	58.9	57.2
3	25.3	-14.3
4	21.9	-14.8
7	5	
1	48.5	-45.1
2	27.0	24.1
3	57.7	59.1
7	6	
2	25.1	21.8
3	13.5	-17.1
4	10.9	-5.5
7	7	
1	46.1	-47.8
7	8	
2	10.9	17.6
8	0	
0	143.4	-153.2
2	46.2	40.8
4	61.0	59.0
6	19.2	-15.0
8	43.0	-38.1
12	39.4	44.4
8	1	
0	46.1	41.3
1	13.0	19.8
2	38.8	-29.3
3	73.6	70.8
5	97.0	-95.4
6	18.9	19.3
7	36.8	-33.0
9	61.4	60.9
10	20.5	-17.6
15	24.3	-18.6
8	2	
0	93.5	-25.4
1	59.1	47.5
3	14.3	12.5
4	48.1	38.1
6	28.1	-25.8
8	21.5	-15.9
10	23.7	17.8
8	3	
0	64.4	58.9
1	39.2	78.1
2	39.4	38.0
3	84.1	78.2
4	60.8	-62.0
8	4	
0	49.9	-54.0
1	25.5	47.1
3	13.3	13.6
4	30.3	40.7
8	5	
0	13.9	17.6
1	58.3	59.8
2	19.5	24.6
3	25.3	12.1
8	6	
0	20.0	-18.5
2	60.5	20.9
4	28.8	44.5
8	7	
0	10.2	11.0
1	18.2	11.0
8	8	
0	18.4	-17.5
9	0	
2	100.0	73.6
4	59.5	-52.9
6	101.6	-109.3
8	26.6	54.3
10	35.3	28.3
12	38.6	-40.9
9	1	
1	42.8	41.2
2	23.2	-25.4
3	22.5	18.6
5	38.4	35.3
6	18.5	-15.8
7	13.3	11.8
9	2	
1	38.1	-24.5
2	150.2	139.9
3	43.3	-24.4
4	43.2	-67.4
5	20.7	-20.5
6	40.4	-66.0
8	37.0	55.4
10	48.2	52.0
12	24.1	-34.4
9	3	
1	23.9	26.0
2	77.0	-69.9
3	15.3	15.1
4	33.8	33.4
9	4	
1	38.4	41.0
2	181.5	217.2
3	38.4	-38.8
4	17.7	-26.9
9	6	
2	62.4	57.0
4	37.8	-30.4
9	8	
2	35.6	38.0
10	0	
0	71.0	73.9
6	13.7	10.8
8	27.5	16.5
10	20.5	-20.4
10	1	
0	38.4	-52.4
1	89.3	40.4
2	33.3	-34.0
3	59.7	60.6
4	15.5	8.1
5	89.3	-83.5
6	22.3	10.1
9	10.2	54.0
11	18.3	-14.2
13	43.5	-25.0
10	2	
0	31.3	32.5
1	25.3	-20.6
3	12.5	-16.2
4	46.5	-45.3
5	14.3	-11.3
6	28.0	22.2
8	17.3	12.1
10	21.3	-27.8
10	3	
0	44.1	-41.4
1	40.7	54.4
2	43.7	41.3
3	63.4	63.4
10	4	
0	34.8	37.6
1	16.7	-20.7
2	37.8	-39.9
3	25.3	-25.1
4	51.9	-52.1
10	5	
0	33.2	34.9
1	51.5	49.1
2	10.9	10.4
3	29.2	30.8
10	6	
0	29.0	30.1
2	20.5	-19.5
4	37.8	-33.7
10	7	
0	14.1	10.7
1	51.0	30.3
3	19.7	40.9
10	8	
0	12.3	14.7
11	0	
2	94.9	89.6
4	17.1	19.7
6	81.9	-81.4
8	50.5	51.8
10	27.4	17.3
12	19.2	-20.1
11	1	
1	63.6	60.7
2	84.5	81.7
3	116.5	-114.0
4	39.0	32.0
5	43.3	-19.3
7	53.5	54.8
8	49.3	-24.7
9	18.5	-18.7
12	27.8	-29.8
11	2	
1	22.3	18.9
2	63.8	63.5
3	39.0	41.9
5	11.9	-7.3
6	54.1	-55.5
7	19.3	19.0
8	25.2	44.2
10	25.7	23.8
11	3	
1	23.9	20.4
2	21.9	-21.8
3	118.6	-109.8
11	4	
1	33.0	36.2
4	45.3	43.4
4	20.9	-19.7
11	5	
1	38.8	37.3
2	35.6	-33.2
3	42.2	-45.6
11	6	
4	20.9	-10.9
11	7	
2	24.3	27.3
3	21.3	-23.9
11	8	
2	21.7	21.0
12	0	
0	164.9	144.3
2	10.9	-6.6
4	117.9	-123.8
6	43.6	42.3
8	81.3	79.2
10	36.6	-57.3
14	10.5	27.4
12	1	
0	37.1	22.0
4	19.5	14.8
12	2	
0	210.4	97.7
1	24.7	-25.8
2	15.5	-4.9
3	15.7	-12.5
4	107.0	-113.5
5	18.5	18.2
6	52.2	55.0
7	18.3	12.0
8	52.7	33.6
10	35.2	-40.3
12	3	
1	29.2	46.1
2	20.9	-18.0
3	23.8	29.2
12	4	
0	75.0	82.4
1	10.5	-11.9
2	25.5	-0.7
3	53.0	-32.7
4	60.3	-69.2
12	5	
0	51.7	55.8
2	24.0	-13.2
4	37.8	-32.4
12	6	
0	37.1	32.1
13	0	
2	81.1	-73.5
4	18.3	18.2
6	45.0	39.3
14	7.6	8.7
13	1	
1	75.8	72.8
3	112.6	-107.0
5	20.8	-17.6
6	23.5	-24.7
7	34.9	37.5
8	24.1	-22.1
11	40.4	-47.0
13	2	
1	43.4	-42.0
2	68.4	-65.8
3	40.0	38.6
4	49.1	50.9
6	28.8	18.2
8	29.4	-30.6
13	3	
1	79.2	72.0
2	25.3	-21.0
3	122.4	-108.1
13	4	
1	20.8	-38.4
2	45.7	-26.8
3	8.9	14.3
13	5	
1	28.8	48.3
2	13.5	-15.0
3	33.5	-38.0
13	6	
2	20.2	-23.6
13	7	
1	18.9	20.8
3	31.8	-33.8
13	8	
2	15.5	-7.8
14	0	
0	129.5	115.1
2	30.6	-31.3
4	77.3	-72.7
6	35.4	33.3
10	34.0	-32.5
14	9.5	9.6
14	1	
0	20.1	-15.7
1	96.4	-89.0
2	39.4	38.2
3	8.9	-14.9
5	86.3	80.0
7	27.2	23.1
9	38.6	-39.8
14	2	
0	33.8	37.8
1	44.5	24.5
3	24.9	20.6
4	37.7	-50.2
6	22.5	6.8
8	32.8	32.2
10	29.5	-23.8
14	3	
1	77.0	-79.1
2	23.3	15.2
3	33.0	-37.2
14	4	
0	45.3	54.9
3	25.3	-26.2
4	35.8	-42.8
14	5	
1	66.4	-84.5
3	47.8	-27.4
14	6	
0	18.7	21.2
14	7	
0	37.2	-34.5
1	11.9	-29.5
14	8	
0	25.9	18.8
15	0	
2	177.2	-186.1
4	43.5	42.4
6	74.8	76.4
8	48.1	-44.4
10	14.0	-25.9
14	6.6	11.4
15	1	
1	27.4	27.8
2	22.7	25.2
6	22.3	23.5
7	84.4	22.8
15	2	
2	105.4	-103.4
4	48.3	50.7
6	56.7	55.3
8	37.2	-38.2
10	29.2	-31.7
15	3	
1	25.9	44.7
2	10.7	4.9
15	4	
1	22.5	-23.7
2	67.6	-74.4
3	15.3	12.7
4	82.9	18.2
15	5	
1	5.6	5.2
3	49.8	38.5
15	6	
4	30.9	-35.1
15	8	
2	22.1	-23.4
16	0	
0	103.4	-104.9
2	21.7	-14.9
4	60.9	55.9
6	16.7	-21.1
8	40.6	-31.7
16	1	
1	102.6	-103.8
3	82.5	-75.5
5	73.8	72.5
9	56.7	-56.4
16	2	
0	33.8	-32.8
2	21.7	22.4
4	43.4	45.9
6	33.6	-34.3
8	20.5	-16.7
10	27.8	26.2
16	3	
0	24.5	-26.8
1	40.6	-43.8
2	21.7	-24.2
3	40.8	-39.8
16	4	
0	7.0	-6.5
4	32.0	25.3
16	5	
1	25.3	-32.5
3	27.5	-20.7
16	6	
0	24.5	-28.5
16	7	
1	18.9	-24.6
16	8	
0	12.3	-8.2
17	0	
2	68.8	-67.2
4	57.5	32.5
6	29.0	30.9
17	1	
1	87.5	-90.2
3	92.3	85.7
5	26.6	22.0
7	65.0	-65.2
11	85.5	29.4
17	2	
1	20.5	-3.7
2	43.9	-43.5
3	18.9	13.3
4	15.3	14.5
6	29.9	22.5
10	29.0	-26.7
17	3	
1	24.5	-23.6
2	17.3	17.5
3	49.7	40.4
17	4	
2	70.6	-75.5
3	31.8	34.3
4	17.7	27.0
17	5	
1	26.1	-32.3
3	24.9	25.8
17	6	
2	21.7	-21.9
17	7	
2	14.7	-16.7
18	0	
0	153.3	-148.5
2	35.1	39.6
4	81.5	82.5
6	32.9	-24.2
8	48.3	-47.3
10	48.2	31.0

Table 3.2

Atomic positions, with estimated standard deviations

(co-ordinates as fractions of cell edge)

Atom	x/a	y/b	z/c
Co	0.08276(7)	0.00950(37)	0.13855(20)
C1	0.0490 (8)	0.0572 (34)	0.3066 (20)
C2	0.0184 (6)	0.0552 (30)	0.2020 (20)
C3	0.0290 (6)	0.1914 (29)	0.1087 (22)
C4	0.0708 (7)	0.2714 (27)	0.1526 (19)
C5	0.0796 (8)	0.1932 (31)	0.2784 (24)
C6	0.1322 (5)	-0.2606 (25)	0.1673 (18)
C7	0.1472 (5)	-0.0761 (28)	0.1337 (20)
C8	0.1306 (7)	-0.0318 (29)	0.0057 (21)
C9	0.0933 (6)	-0.1307 (30)	-0.0132 (20)
C10	0.0868 (5)	-0.2424 (28)	0.1048 (21)
C11	0.1668 (6)	-0.3982 (23)	0.1249 (18)
C12	0.1945 (5)	-0.4714 (25)	0.2134 (16)
C13	0.2249 (6)	-0.6045 (31)	0.1789 (20)
C14	0.2267 (5)	-0.6630 (27)	0.0515 (20)
C15	0.1967 (6)	-0.5919 (31)	-0.0383 (17)
C16	0.1666 (6)	-0.4649 (28)	-0.0016 (18)

Table 3.3

Anisotropic Thermal Parameters with estimated standard deviations.

The temperature factor (T) is defined as:-

$$T = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)}$$

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Co	0.00118 (1)	0.0208 (4)	0.0073 (2)	-0.0060(12)	-0.0010 (1)	0.0009 (3)
C1	0.00300(36)	0.0485(68)	0.0126(21)	0.0034(89)	0.0021(15)	0.0088(26)
C2	0.00133(22)	0.0410(59)	0.0169(23)	-0.0052(85)	0.0039(12)	0.0015(18)
C3	0.00166(24)	0.0373(52)	0.0188(27)	0.0073(87)	0.0019(15)	0.0051(19)
C4	0.00330(34)	0.0210(38)	0.0128(21)	0.0098(78)	0.0069(15)	0.0053(21)
C5	0.00248(33)	0.0420(58)	0.0223(31)	-0.0400(91)	-0.0010(18)	0.0100(26)
C6	0.00141(20)	0.0174(29)	0.0139(20)	0.0038(78)	-0.0007(11)	0.0011(17)
C7	0.00085(15)	0.0373(46)	0.0180(23)	-0.0246(82)	0.0033(12)	0.0006(16)
C8	0.00272(31)	0.0320(57)	0.0174(23)	0.0293(90)	0.0074(15)	0.0075(25)
C9	0.00133(22)	0.0450(57)	0.0127(22)	-0.0048(76)	0.0027(12)	0.0061(20)
C10	0.00104(18)	0.0270(34)	0.0202(24)	-0.0169(80)	-0.0004(13)	-0.0029(20)
C11	0.00157(20)	0.0196(34)	0.0120(21)	0.0069(68)	0.0024(12)	0.0007(16)
C12	0.00142(20)	0.0265(45)	0.0126(18)	0.0231(73)	0.0019(10)	0.0047(17)
C13	0.00158(24)	0.0400(52)	0.0154(24)	0.0091(81)	0.0019(13)	-0.0018(21)
C14	0.00103(20)	0.0284(43)	0.0189(27)	0.0080(72)	0.0021(13)	-0.0019(16)
C15	0.00219(28)	0.0355(49)	0.0087(18)	0.0035(72)	0.0002(12)	0.0015(22)
C16	0.00175(23)	0.0334(56)	0.0131(18)	-0.0160(79)	0.0025(12)	0.0051(19)

Table 3.4.

Interatomic distances and angles (with e.s.d's)

(i) cobalt-carbon distances

Atoms	Interatomic distance (Å)	e.s.d. (Å)	Atoms	Interatomic distance (Å)	e.s.d. (Å)
Co-C1	2.086	.023	Co-C6	2.563	.018
Co-C2	2.055	.021	Co-C7	2.021	.019
Co-C3	2.146	.022	Co-C8	2.031	.022
Co-C4	2.054	.021	Co-C9	1.972	.021
Co-C5	2.059	.024	Co-C10	1.977	.020

(ii) π-cyclopentadienyl system

Atoms	Interatomic distance (Å)	e.s.d. (Å)	Atoms	Angle (°)	e.s.d (°)
C1-C2	1.439	.031	C5-C1-C2	104.3	1.8
C2-C3	1.481	.030	C1-C2-C3	112.4	1.8
C3-C4	1.461	.030	C2-C3-C4	105.2	1.7
C4-C5	1.495	.031	C3-C4-C5	105.4	1.7
C5-C1	1.416	.033	C4-C5-C1	112.2	1.8

Table 3A(contd.)

(iii) cyclopentadiene system

Atoms	Interatomic distance (Å)	e.s.d. (Å)	Atoms	Angle (°)	e.s.d. (°)
C6–C7	1.532	.026	C10–C6–C7	93.9	1.5
C7–C8	1.491	.029	C6–C7–C8	109.4	1.5
C8–C9	1.359	.030	C7–C8–C9	106.0	1.6
C9–C10	1.538	.030	C8–C9–C10	107.0	1.7
C10–C6	1.506	.027	C9–C10–C6	107.7	1.5

(iv) phenyl ring

C11–C12	1.373	.025	C16–C11–C12	120.0	1.5
C12–C13	1.412	.027	C11–C12–C13	120.0	1.6
C13–C14	1.433	.029	C12–C13–C14	120.0	1.5
C14–C15	1.418	.028	C13–C14–C15	119.8	1.7
C15–C16	1.380	.028	C14–C15–C16	119.1	1.6
C16–C11	1.445	.026	C15–C16–C11	121.0	1.6

(v) miscellaneous

C6–C11	1.544	.025	C10–C6–C11	121.8	1.4
			C11–C6–C7	112.0	1.4
			C12–C11–C6	118.6	1.4
			C16–C11–C6	121.0	1.4

Table 3.5

Calculated Hydrogen Positions

Atom	$^x/_a$	$^y/_b$	$^z/_c$
H1	0.0486	-0.0272	0.3871
H2	-0.0100	-0.0334	0.1953
H3	0.0123	0.2227	0.0214
H4	0.0890	0.3720	0.1027
H5	0.1072	0.2278	0.3393
H6	0.1291	-0.3054	0.2627
H7	0.1763	-0.0199	0.1795
H8	0.1509	0.0526	-0.0524
H9	0.0740	-0.1205	-0.0988
H10	0.0608	-0.3367	0.1223
H12	0.1937	-0.4257	0.3090
H13	0.2473	-0.6582	0.2484
H14	0.2496	-0.7646	0.0234
H15	0.1975	-0.6376	-0.1340
H16	0.1441	-0.4112	-0.0711

Table 3.6.

Intermolecular Contacts

Atom of reference molecule	Atom in neighbouring molecule	Distance (Å)
C1	C3 $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3.76
	H3 $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3.05
	H16 $(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$	3.30
	H2 $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.36
	H4 $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3.42
	H10 $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.44
C2	C3 $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3.73
	C4 $(-x, -\frac{1}{2}+y, \frac{1}{2}-z)$	3.76
	H9 $(-x, -y, -z)$	3.00
	H10 $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.12
	H3 $(-x, -y, -z)$	3.33
	H2 $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.36
C3	C9 $(-x, -y, -z)$	3.79
	H2 $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.03
	H9 $(-x, -y, -z)$	3.10
	H1 $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	3.16
	H2 $(-x, -y, -z)$	3.50
C4	H2 $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	2.86
	H10 $(x, 1+y, z)$	3.05
C5	H2 $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	2.96
	H16 $(x, -\frac{1}{2}-y, \frac{1}{2}+z)$	3.31
	H3 $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3.34
	H8 $(x, \frac{1}{2}-y, \frac{1}{2}+z)$	3.40

Table 6 (contd.)

C6	C9	$(x, -\frac{1}{2}-y, \frac{1}{2}+z)$	3.70
	H9	$(x, -\frac{1}{2}-y, \frac{1}{2}+z)$	3.17
	H4	$(x, -1+y, z)$	3.18
C7	H16	$(x, -\frac{1}{2}-y, \frac{1}{2}+z)$	3.16
	H15	$(x, -\frac{1}{2}-y, \frac{1}{2}+z)$	3.33
	H13	$(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3.42
C8	C12	$(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$	3.65
	H12	$(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$	2.83
	H6	$(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$	2.88
	H5	$(x, \frac{1}{2}-y, -\frac{1}{2}+z)$	3.02
C9	H6	$(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$	2.65
	H1	$(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$	3.13
	H3	$(-x, -y, -z)$	3.21
	H2	$(-x, -y, -z)$	3.39
C10	H4	$(x, -1+y, z)$	2.97
	H1	$(x, -\frac{1}{2}-y, -\frac{1}{2}+z)$	3.14
	H3	$(-x, -y, -z)$	3.24
	H9	$(x, -\frac{1}{2}-y, \frac{1}{2}+z)$	3.36
C11	C14	$(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3.72
	H14	$(\frac{1}{2}-x, \frac{1}{2}+y, z)$	2.89
	H4	$(x, -1+y, z)$	2.92
C12	C13	$(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3.72
	C14	$(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3.75
	H8	$(x, -\frac{1}{2}-y, \frac{1}{2}+z)$	2.88
	H13	$(\frac{1}{2}-x, \frac{1}{2}+y, z)$	2.99
	H14	$(\frac{1}{2}-x, \frac{1}{2}+y, z)$	3.07
	H15	$(x, -1\frac{1}{2}-y, \frac{1}{2}+z)$	3.42

Table 6 (contd.)

C13	H15 $(x, -1\frac{1}{2} - y, \frac{1}{2} + z)$	2.93
	H7 $(\frac{1}{2} - x, -\frac{1}{2} + y, z)$	3.00
	H14 $(\frac{1}{2} - x, \frac{1}{2} + y, z)$	3.19
C14	H14 $(\frac{1}{2} - x, \frac{1}{2} + y, z)$	3.16
	H8 $(x, -1 + y, z)$	3.33
	H7 $(\frac{1}{2} - x, -\frac{1}{2} + y, z)$	3.37
	H7 $(x, -1 + y, z)$	3.41
C15	H14 $(\frac{1}{2} - x, \frac{1}{2} + y, z)$	3.05
	H8 $(x, -1 + y, z)$	3.06
	H5 $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$	3.14
	H7 $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$	3.19
	H13 $(x, -1\frac{1}{2} - y, -\frac{1}{2} + z)$	3.34
	H13 $(\frac{1}{2} - x, -1 + y, -\frac{1}{2} + z)$	3.41
C16	H4 $(x, -1 + y, z)$	2.85
	H14 $(\frac{1}{2} - x, \frac{1}{2} + y, z)$	2.94
	H5 $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$	3.18
	H7 $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$	3.42
	H6 $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$	3.45
H1	H10 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.75
	H3 $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$	2.82
	H9 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.82
	H4 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.86
	H16 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.90
H2	H9 $(-x, -y, -z)$	2.46
	H3 $(-x, -y, -z)$	2.74
	H10 $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$	2.89

Table 6 (contd.)

H3	H10 $(-x, -y, -z)$	2.80
	H9 $(-x, -y, -z)$	2.80
H4	H10 $(x, 1 + y, z)$	2.40
H5	H8 $(x, \frac{1}{2} - y, \frac{1}{2} + z)$	2.42
	H15 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.78
	H16 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.84
H6	H9 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.29
	H16 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.48
	H8 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.82
H7	H15 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.42
	H13 $(\frac{1}{2} - x, \frac{1}{2} + y, z)$	2.61
	H15 $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$	2.88
H8	H12 $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$	2.18
	H15 $(x, 1 + y, z)$	2.89
H12	H13 $(\frac{1}{2} - x, \frac{1}{2} + y, z)$	2.78
H13	H15 $(x, -1\frac{1}{2} - y, \frac{1}{2} + z)$	2.50

Table 3·7 Root mean square amplitudes and direction cosines of the atomic vibration ellipsoids.

(d.c's are referred to the orthogonal axes a, b, c of the crystal.)

Atom	$\sqrt{\overline{u^2}_{max.}}$ (d.c's of major axis)	$\sqrt{\overline{u^2}_{med.}}$ (d.c's of median axis)	$\sqrt{\overline{u^2}_{min.}}$ (d.c's of minor axis)
Co	0.22	0.20	0.15
	(-0.095,-0.911, 0.402)	(0.905, 0.089, 0.417)	(-0.416, 0.403, 0.815)
C1	0.32	0.30	0.22
	(-0.459,-0.869,-0.182)	(0.853,-0.469, 0.183)	(-0.248,-0.072, 0.966)
C2	0.30	0.27	0.17
	(0.205,-0.848, 0.489)	(0.454, 0.525, 0.720)	(0.867,-0.074,-0.493)
C3	0.31	0.26	0.20
	(0.437, 0.722, 0.537)	(-0.142,-0.535, 0.833)	(0.888,-0.440,-0.131)
C4	0.36	0.19	0.17
	(0.841, 0.283, 0.461)	(0.392,-0.906,-0.160)	(-0.372,-0.315, 0.873)
C5	0.40	0.27	0.14
	(0.379, 0.700,-0.605)	(0.814, 0.060, 0.577)	(-0.440, 0.712, 0.547)
C6	0.24	0.21	0.18
	(-0.187, 0.206, 0.960)	(0.884, 0.462, 0.073)	(-0.428, 0.863,-0.269)
C7	0.33	0.22	0.12
	(0.130,-0.710, 0.692)	(0.526, 0.641, 0.559)	(0.040,-0.292,-0.457)
C8	0.39	0.22	0.16
	(0.611, 0.525, 0.593)	(-0.760, 0.597, 0.255)	(-0.220,-0.607, 0.764)
C9	0.32	0.25	0.15
	(0.362, 0.932,-0.018)	(0.470,-0.165, 0.867)	(0.805,-0.323,-0.498)

(continue

Table 7 (contd.)

C10	0.31	0.22	0.16
	(-0.065, 0.534,-0.843)	(0.550,-0.686,-0.477)	(0.833, 0.494, 0.249)
C11	0.25	0.20	0.18
	(0.618, 0.360, 0.699)	(0.656,-0.727,-0.206)	(-0.434,-0.585, 0.685)
C12	0.31	0.19	0.13
	(0.381, 0.695, 0.610)	(0.890,-0.095,-0.447)	(0.253,-0.713, 0.654)
C13	0.30	0.26	0.20
	(0.060,-0.913,-0.404)	(0.605,-0.289, 0.742)	(0.794, 0.289,-0.535)
C14	0.29	0.24	0.16
	(-0.143,-0.400,-0.905)	(0.386,-0.865, 0.321)	(0.911, 0.304,-0.279)
C15	0.28	0.25	0.19
	(0.501, 0.858, 0.113)	(0.865,-0.499,-0.049)	(-0.014,-0.122, 0.992)
C16	0.30	0.26	0.14
	(-0.335,-0.848, 0.411)	(0.746, 0.027, 0.665)	(-0.575, 0.529, 0.623)

CHAPTER IV

THE CRYSTAL AND MOLECULAR STRUCTURE OF π-CYCLOPENTADIENYL-HEXAKIS(TRIFLUOROMETHYL)BENZENE-RHODIUM.

4.1. Introduction

The first π-arene transition metal compounds prepared were formulated as polyphenylchromium compounds e.g. $(C_6H_5)_5 Cr^+Br^-$ (Hein, 1919) but were not recognised as π-complexes until Zeiss and Tsutsui (1954) suggested their possible similarity to ferrocene. The first simple π-benzene complex to be prepared was $(\pi\text{-}C_6H_6)_2Cr$ (Fischer and Hafner, 1955). Preliminary crystal data were reported by Weiss and Fischer (1956) and, to date, two separate structural studies have been reported. Jellinek (1960) reported that the double bonds were localised in the benzene nuclei, but a more extensive analysis (Cotton, Dollase and Wood, 1963) suggests that the carbon-carbon bondlengths are, in fact equal.

Structural studies on the molecular complexes $Ag\ C\ell O_4.C_6H_6$ (Smith and Rundle, 1958) and $CuA\ell C\ell_4.C_6H_6$(Amma, Turner and Vranka, 1963) indicate that the benzene entity is distorted towards the cyclohexatriene system, but, in the absence of spectroscopic evidence for the presence of a localized system, it is assumed that these distortions result from lattice effects.

The present three-dimensional single crystal X-ray structural analysis of π-cyclopentadienyl-hexakis(trifluoromethyl)benzenerhodium was thus undertaken to ascertain whether the fluorine magnetic resonance spectrum, suggesting three different environments for fluorine nuclei (Dickson and Wilkinson, 1963) was the result of localization of charge in the benzene skeleton, or whether this effect was due to other factors.

4.2. Experimental

π-cyclopentadienyl-hexakis(trifluoromethyl)benzenerhodium was prepared (in approximately equal yield with π-cyclopentadienyl-tetrakis(trifluoromethyl)cyclopentadienonerhodium) by the reaction of hexafluorobut-2-yne and π-cyclopentadienyl rhodium dicarbonyl at elevated temperature and pressure (Dickson and Wilkinson, 1963), and single crystals were readily obtained by evaporation of a solution in light petroleum ether (b.p. 30-40°C). The pale-yellow, air-stable, monoclinic crystals have well developed (101) and small, but characteristic (001) faces.

Intensity photographs were taken with the crystal mounted along c, using a Buerger precession camera and Ilford Industrial G X-ray films. Molybdenum K_α radiation ($\bar{\lambda} = 0.7107$ Å) was used to collect data for the $\{h0\ell\}$, $\{h1\ell\}$, $\{h2\ell\}$, $\{h3\ell\}$, $\{h4\ell\}$, $\{0k\ell\}$, $\{1k\ell\}$ and $\{2k\ell\}$ zones. A crystal of approximately (± 30%) spherical habit and diameter 0.2 mm. was used. No corrections were made for absorption.

The unit cell parameters, obtained by a least-squares analysis of high-angle precession data are:-

$a = 9.48 \pm 0.02$ Å

$b = 12.59 \pm 0.02$ Å

$c = 17.79 \pm 0.03$ Å

$\beta = 114.75 \pm 0.1^\circ$

The observed density, $\rho(obs) = 2.27 \pm 0.02$ gm. cm.$^{-3}$, measured by flotation in Rohrbach's solution, is in good agreement with the calculated value, $\rho(calc) = 2.255$ gm. cm.$^{-3}$ where $V = 1928$ Å^3, $Z = 4$ and $M = 654$ for $C_5H_5Rh(CF_3)_6C_6$.

Systematic absences $h0\ell$ for $\ell = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely assign the spacegroup as $P2_1/c$ (no. 14; C^5_{2h}).

All intensities were estimated visually using a standard calibrated strip.

4.3. Solution of the Phase Problem

The spacegroup for crystals of π-$C_5H_5Rh(CF_3)_6C_6$ is $P2_1/c$ which has the following four equipoints:-

$x,$	$y,$	z
$-x,$	$-y,$	$-z$
$x,$	$\frac{1}{2}-y,$	$\frac{1}{2}+z$
$-x,$	$\frac{1}{2}+y,$	$\frac{1}{2}-z$

Considering the metal atom alone, there are twelve vectors relating the four rhodium atoms in the unit cell. These are given below (m = the multiplicity of the vector peak):

m = 2	0	$\frac{1}{2} + 2y$	$\frac{1}{2}$
	0	$\frac{1}{2} - 2y$	$\frac{1}{2}$
	$2x$	$\frac{1}{2}$	$\frac{1}{2} + 2z$
	$-2x$	$\frac{1}{2}$	$\frac{1}{2} - 2z$
m = 1	$2x$	$2y$	$2z$
	$2x$	$-2y$	$2z$
	$-2x$	$2y$	$-2z$
	$-2x$	$2y$	$-2z$

Two dimensional Patterson syntheses, P(UOW) and P(OVW) failed to locate the rhodium position accurately but showed vector peaks consistent with approximate fractional coordinates $\sim\frac{1}{4}$, 0.14, $\sim\frac{1}{4}$ for the rhodium position. The three-dimensional synthesis P(UVW) confirmed these conclusions, but failed successfully to resolve overlapping vectors with pseudo-special coordinates. There are four possibilities for the rhodium in terms of Δ, the distance of a coordinate from the special position $\frac{1}{4}$, y, $\frac{1}{4}$. These are:-

(i) $\frac{1}{4} + \Delta x$, 0.14, $\frac{1}{4} + \Delta z$

(ii) $\frac{1}{4} - \Delta x$, 0.14, $\frac{1}{4} - \Delta z$

(iii) $\frac{1}{4} + \Delta x$, 0.14, $\frac{1}{4} - \Delta z$

(iv) $\frac{1}{4} - \Delta x$, 0.14, $\frac{1}{4} + \Delta z$

It can be shown that (i) and (ii) are identical in their phasing of the structure amplitudes and that (iii) and (iv) are, likewise, identical in this respect, requiring only a shift of origin when defining the unit cell. Consequently, the problem can easily be solved by trial and error techniques. This would be, however, an arbitrary and time-consuming method. An alternative approach involves the use of the "Patterson sharpening function". Each of the observed intensities is related to the atomic position by:-

$$|F(hk\ell)|^2 = |\sum_{j=o}^{j=n} f_{j,\theta(hk\ell)} \exp - 2\pi i(hx + ky + \ell z)|^2$$

for a stationary atom.

However, at room temperature the atomic scattering factor, f, is modified by a temperature factor:-

$$f_{j,\theta} \text{ becomes } f_{j,\theta} \exp (- B\sin^2\theta/\lambda^2)$$

Hence, if the temperature factor is artificially removed, the atomic profiles become less diffuse, and a Patterson synthesis based on the "sharpened" planes shows interatomic vectors with a much enhanced resolution between neighbouring peaks. The temperature factor is removed by applying the formula:-

$$F(hk\ell, \text{sharpened}) = F(hk\ell, \text{obs}) \exp B\sin^2\theta/\lambda^2$$

where B is the (estimated) overall isotropic temperature factor for the molecule. A more sophisticated treatment, involving sharpening via temperature factor removal <u>and</u> gradient steepening has been described (Jacobson, Wunderlich and Lipscomb, 1961).

Examination of a Patterson synthesis P(UVW) sharpened by this procedure revealed a set of resolved vectors consistent with a rhodium position at $x = 0.255$, $y = 0.142$, $z = 0.239$.

4.4. The Determination and Refinement of the Structure

The analysis commenced using a total of 1622 independent reflexions from the {h0ℓ}, {h1ℓ}, {h2ℓ}, {h3ℓ}, {h4ℓ}, and {0kℓ} zones. Structure factors calculated from the rhodium contribution only had a discrepancy index R ($= \Sigma|F_{obs} - F_{calc}|/\Sigma F_{obs}$) of 0.49. The Fourier synthesis, $\rho(xyz)$, based on these structure factors, revealed the positions of the six carbon atoms constituting the benzene ring, and four of the six trifluoromethyl groups (although in each case the carbon position of the CF_3- group could not clearly be seen, and was only deduced from its tetrahedral environment). Structure factors, phased now by the rhodium, ten carbon and twelve fluorine atoms, showed an improved discrepancy index, R = 0.37, and a three-dimensional Fourier synthesis, using these as coefficients, revealed the positions of the remaining two trifluoromethyl groups and the approximate location of the π-cyclopentadienyl ligand. The first complete structure factor calculation phased by all atoms (except hydrogens) has a discrepancy index R = 0.30 which reduced to 0.224 after a single cycle of least-squares refinement with isotropic temperature factors, and thence to 0.189 after one cycle of positional and anisotropic thermal parameter refinement.

A calculation of the geometry then revealed that refinement had resulted in unacceptable bondlengths in the π-cyclopentadienyl ring (between 0.9 and 2.2 Å). A subsequent difference Fourier synthesis, based on structure factors phased by all atoms other than those in the π-cyclopentadienyl system, revealed the true positions of the carbon atoms in this ligand. With these positions corrected the discrepancy index reduced at once to R = 0.152, and thence to 0.116 in two further cycles of anisotropic refinement.

At this stage it became apparent that the coverage of y-data was inadequate and reflexions for the {1kℓ} and {2kℓ} zones were added, giving a total of 2128 independent reflexions. That the lack of y-data had resulted in slightly erroneous y-coordinates for some atoms was immediately seen by the rise in the discrepancy index to 0.133. Refinement now proceeded painfully slowly (each cycle taking approximately 4¼ hours of computer time). Three cycles of refinement reduced R to 0.119, and, after carefully rescaling the eight constituent zones, a further seven cycles of refinement reduced R to 0.107. Bondlengths at this point in the refinement were far from satisfactory (ranging from 1.23 → 1.44 Å in the π-cyclopentadienyl ligand, and as high as 1.58 Å for carbon-fluorine bonds).

The weighting scheme for the refinement was changed from unit weights to reciprocal weights, but three cycles of refinement using this scheme failed to improve any of the bondlengths, and did, in fact, nothing noticeable except increase R to 0.126.

It was thought that most of the problems in the refinement were simply due to the approximations involved in the computer program used (i.e. the complete matrix is broken down into blocks and a system of block-diagonal refinement is used in which no cross-terms between atoms are considered and no positional - anisotropic thermal parameter cross-terms are considered even when involving the same atom). Consequently, even though the fluorine atoms were known to be highly anisotropic in their thermal motion, the refinement was continued using isotropic temperature factors since the block-diagonal refinement scheme for isotropic temperature factors does, in fact, contain positional-vibrational cross-terms for any given atom. Five cycles of isotropic refinement proved that the non-refinable cross-terms arose from other sources, because although the isotropic refinement started at R = 0.19 and improved at R = 0.17, geometric calculations showed no improvement in bond-lengths.

Finally, positional and anisotropic thermal parameter refinement was continued using the "logical weighting scheme" -

$$\omega = \frac{1}{1 + \left(\frac{|F_{obs}| - 5}{7}\right)^2}$$

This gives a weight of approximately 0.2 for very intense reflexions a weight of ca. 0.5 for very weak reflexions and a maximum weighting of up to 1.0 for reflexions in the most-accurate-to-read range of

20 - 80.

Using the above weighting scheme, refinement started at $R = 0.120$. The π-cyclopentadienyl was put into the refinement scheme with (calculated) acceptable bondlengths and was not refined for three cycles while the reliability index, R, dropped to 0.110. Nine planes, apparently suffering from extinction were omitted from the refinement scheme. Adjustment of parameters of the π-cyclopentadienyl group was finally allowed, the first cycle giving a discrepancy index $R = 0.098$ which reduced in four further cycles to the final value of 0.096.

The course of the refinement is outlined in Table 4.1; observed and calculated structure factors are shown in Table 4.2 (the F_{calc}'s do not include contributions from the five hydrogen atoms in each molecule). The final atomic coordinates and their estimated standard deviations (e.s.d.'s) are collected in Tables 4.3. and 4.3a; anisotropic thermal parameters are listed in Table 4.4. A composite electron density synthesis is shown in Figure 4.1.

4.5. The Molecular Structure

Intramolecular bond-lengths and -angles (with their e.s.d.'s) are collected in Tables 4.5. and 4.6; Figure 4.2 shows the numbering scheme for the molecule.

The structural details indicate that the benzene nucleus is present as a localized configuration in which only four of the

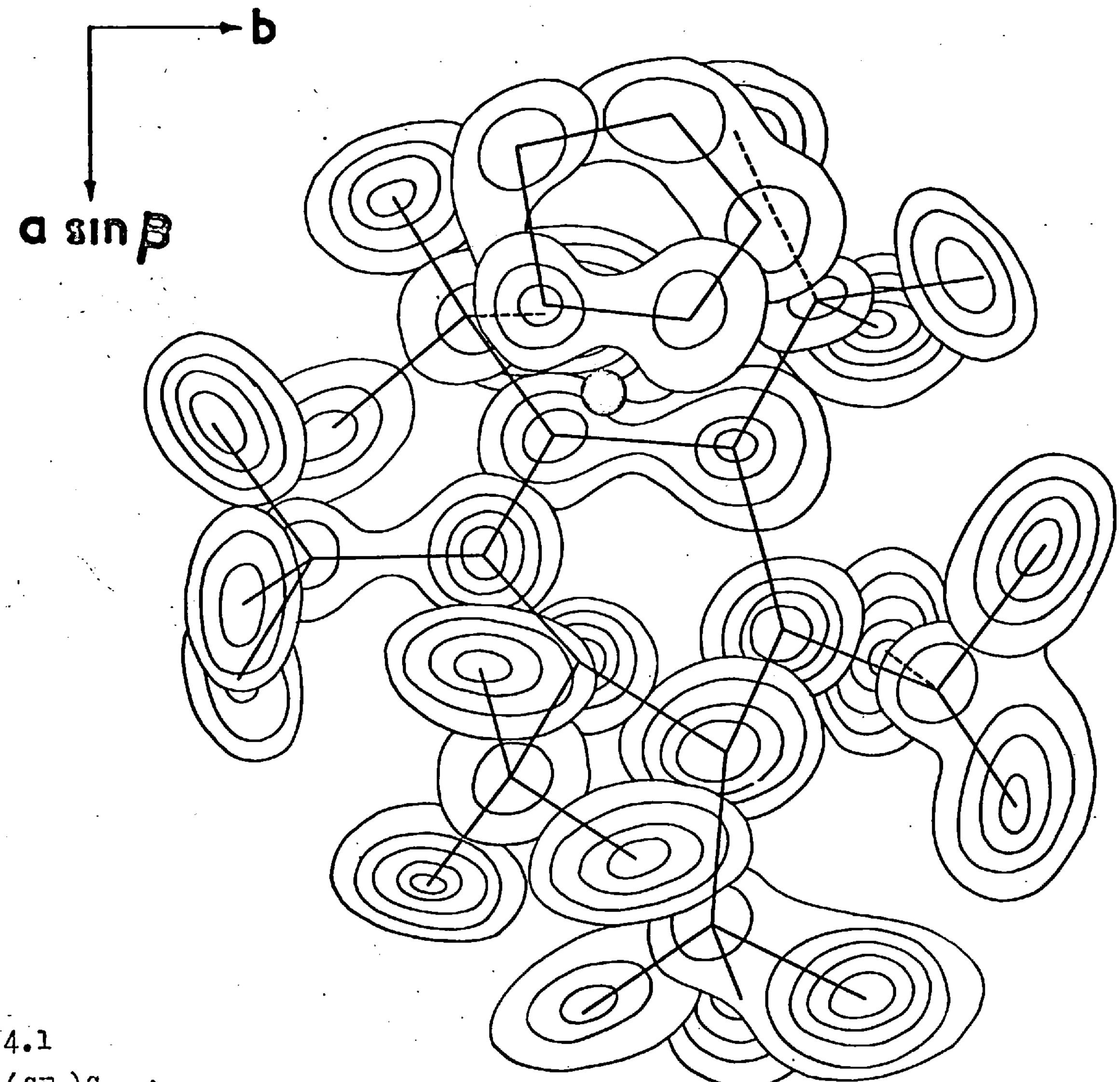


Figure 4.1

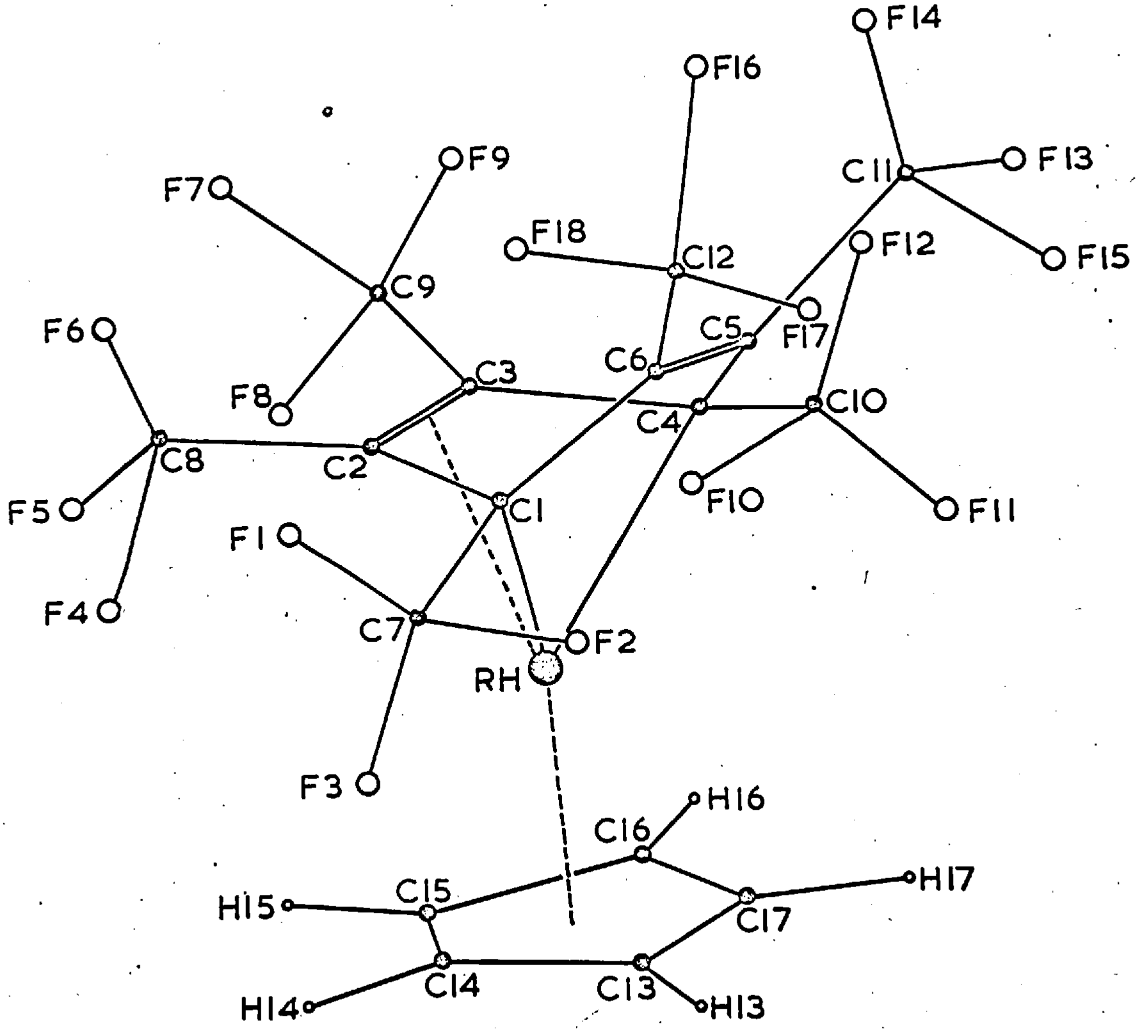
π-$C_5H_5Rh(CF_3)C_6$:

Composite Electron Density Synthesis , projected down 'c'.

Contours are shown at one electron intervals , the lowest being 2e.Å^{-3}

Figure 4.2.

Numbering of Atoms in the Molecule.



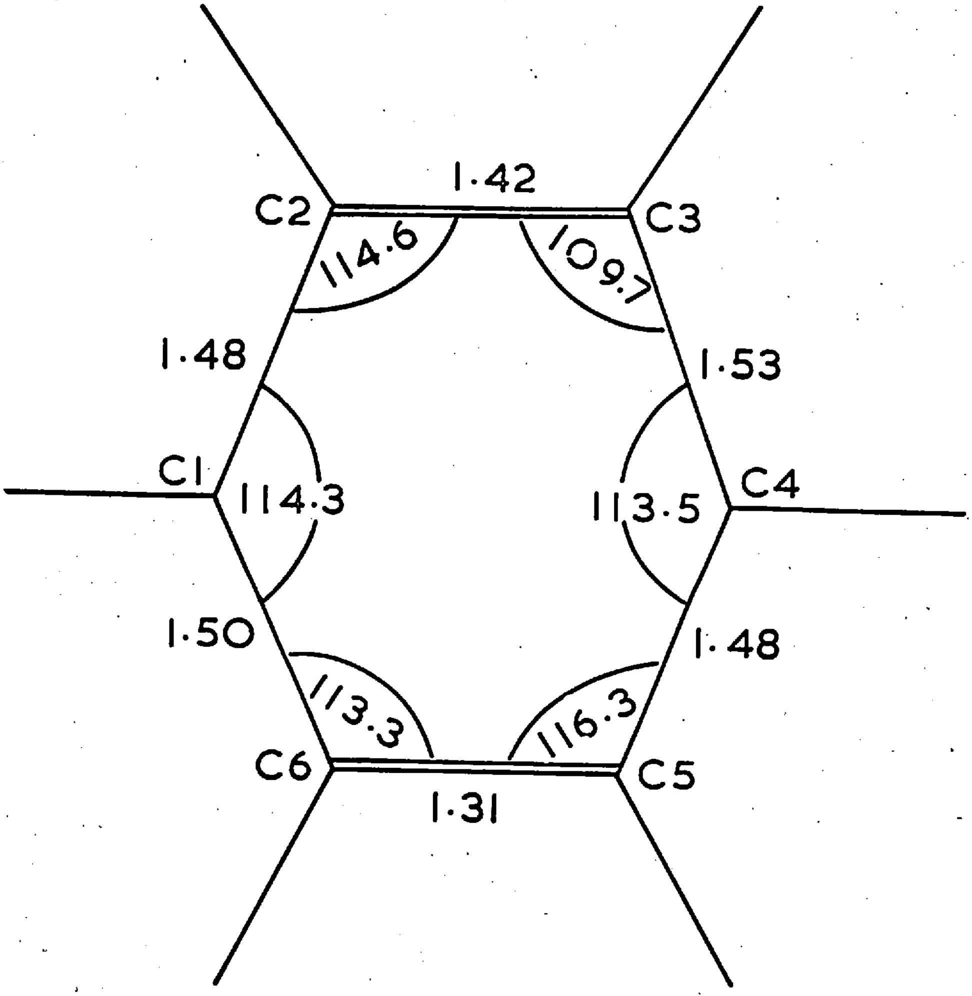
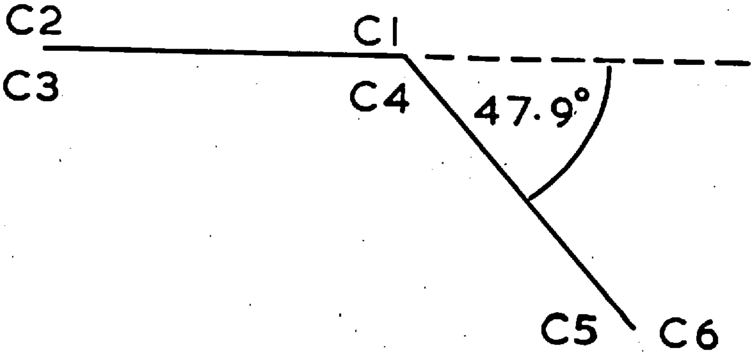


Figure 4.3.

π-$C_5H_5Rh(CF_3)_6C_6$:

Bondlengths in

the Benzene Ligand.



six atoms are involved in the bonding to the rhodium ion. This is demonstrated by:-

(i) The non-planarity of the benzene nucleus. Atoms C1, C2, C3 and C4 form a plane (r.m.s. deviation 0.015 Å); the direction cosines to the normal are 0.3380, 0.0176, 0.9410 (referred to the orthogonal axes a, b*, csinβ). The normal to the plane containing C4, C5, C6 and C1 has direction cosines -0.1386, -0.6184, 0.7736, the r.m.s. deviation from planarity of these four atoms being 0.006 Å. The plane containing C5 and C6 is thus tilted from the plane of the four atoms (C1, C2, C3, C4) bonded to the rhodium ion by an angle of 47.9°. This severe distortion from planarity can be thought of as arising via a change of C1 and C4 from an sp^2 valence state in the free ligand to an sp^3 state in the present complex.

(ii) A detailed study of the bondlengths in the four carbon atom system bonded to the metal shows that the bonds C1 - C2 and C3 - C4 average 1.50 Å in length (which is in good agreement with the accepted value of 1.51 Å for a bond involving an sp^2 and an sp^3 hybridized carbon atom) whereas C2 - C3 is much shorter (1.42 Å) and in the range expected (Dahl and Wei, 1963) for an olefinic bond coordinated to a transition metal. In contrast to this, the bond C5 - C6 (1.31 Å) is in reasonable agreement with the expected value of 1.34 Å for a non-coordinated olefinic linkage. The remaining two bonds in the ring i.e. C1 - C6 and C4 - C5 average 1.49 Å in length, consistent, once again with the accepted sp^2 - sp^3 value.

(iii) The distance C1 - C4 is 2.56 ± 0.02 Å, which is considerably less than the value for the bisector of a regular benzene ring (2.80 Å). This indicates that the atoms C1 and C4 have been pulled closer together by the localized Rh - C1 and Rh - C4 interactions. This view is substantiated by an inspection of the interior angles in the benzene ring (see Figure 4.3). The angles C1 - C2 - C3, C2 - C3 - C4, C4 - C5 - C6 and C5 - C6 - C1 are all less than the value of 120° predicted for sp^2 hybridized carbon atoms; similarly, the angles at C1 and C4 have been increased from the tetrahedral value (109.5°) to 114.3° and 113.5° respectively.

The "pulling together" of atoms C1 and C4 seems an altogether energetically unfavourable process and must be accompanied and counterbalanced by an energetically favourable process which, in this case, can only be the increasing of the rhodium-carbon overlap integrals for C1 and C4.

The bonding from the rhodium atom to the benzene ring is, in valence-bond terms, formally represented by two σ-bonds and one π-bond. The mean distance of the σ-bonded carbon atoms (C1 and C4) from the rhodium ion is 2.13 Å, whereas the π-bonding carbon atoms (C2 and C3) are 2.08 Å from the metal. The large angle of distortion in the benzene ring results in the remaining atoms (C5 and C6) being 1.00 Å above the plane of the four bonded atoms and 3.03 Å from the rhodium ion, at which distance there is, of course, no possibility of significant interaction with the metal.

The general conformation of the benzene ring in this compound is remarkably similar to the so-called "Dewar structure" for benzene which has recently been found to exist, in a non-planar form, as the separate entity bicyclo[2,2,0]hexadiene (van Tameten and Pappas, 1963). The electronic, rather than steric, nature of the large angle of distortion in the benzene ring is best indicated by comparing the angle of distortion of the cyclohexadiene portion of $C_6F_8Fe(CO)_3$ (Chapter V) which is 47.3° (when there is no particular steric requirement for the ligand to lose its planarity) with the present value of 47.9°.

The rhodium atom may be regarded as having an oxidation state of +3, with a d^6 electronic configuration, and is in a trigonally distorted octahedral environment (the six "points of attachment" being the π- and two σ-bonds from the benzene nucleus and three bonds to the formally tri-dentate π-cyclopentadienyl ligand).

The plane of the atoms C1, C2, C3, C4 is 1.67 Å above the metal; that this value is considerably less than that of 1.85 Å for the distance of the π-cyclopentadienyl ring below the metal is, to some extent, an effect of ring size and one would predict that the analogous cyclopentadiene (rather than benzene) complex would not show so great a disparity in the two perpendicular metal-ring distances.

The π-cyclopentadienyl ligand is planar (with r.m.s. deviation 0.004 Å); the normal to this plane has direction cosines 0.2933, -0.1265, 0.9479. The π-cyclopentadienyl group and the "butadiene" system C1, C2, C3, C4 are in a staggered conformation (as evidenced by the inter-annular distances, Table 4.8), but are not strictly parallel, the angle between the two planes being 8.9°. The mean rhodium-carbon bondlength in the π-cyclopentadienyl ring is 2.20 Å. The rhodium carbon distances vary systematically around the ring with C17 the closest (2.166 Å) and C14 the furthest (2.232 Å) from the metal. This distortion, which is on the border-line of statistical significance, is consistent with the close carbon-fluorine and hydrogen-fluorine contacts involving C14 and H14 (F3-C14 = 2.90 Å; F3-H14 = 2.52 Å). Since the other two most important inter-annular contacts involve C16 and H16 (F10-C16 = 2.92 Å; F10-H16 = 2.36 Å) it is not surprising that the section of the ring C14-C15-C16 is the furthest from the metal. It is interesting to note that the shortest bond in the π-cyclopentadienyl ligand (1.34 Å) involves the carbon atoms closest to the metal, neither of which are severly affected by inter-annular contacts. Again, the two longest bonds (1.44 Å and 1.41 Å) are C15-C16 and C14-C15 respectively i.e. those atoms which are being "pushed away" from the metal.

Finally, the trifluoromethyl groups must be considered. The extreme difficulty of obtaining satisfactory bondlengths and bond-angles is evidenced by Tables 4.5 and 6. The final carbon-fluorine bondlengths vary between 1.11 Å and 1.50 Å and the F-C-F angles between 96.3° and 120.5°. The estimated standard deviations average about 0.03 Å and 2° for carbon-fluorine bondlengths and angles. What, then, is the cause of these large discrepancies in the observed carbon-fluorine bondlengths? It may, in fact, be caused by a combination of the following factors:-

(i) The trifluoromethyl groups are probably undergoing large librational motions (see section 4.6). The computer program available describes the anisotropic thermal motion of an atom in terms of an ellipsoid of vibration. Since the trifluoromethyl groups are librating about the benzene-carbon bond, the time averaged electron density for a fluorine atom will be distributed about the arc of a circle rather than about a major axis of an ellipsoid. Consequently there are systematic errors in the structure factor calculation which may result in some atoms being (slightly) incorrectly positioned.

(ii) The refinement was not performed using a full-matrix scheme. Consequently, any interatomic or positional-vibrational cross-terms arising in the least-squares refinement matrix are

are neglected. In the present case it is almost certain, partly as a corollary to (i), that some, at least, of these cross-terms are important.

(iii) As a result of using a block-diagonal matrix, the actual standard deviations are calculated from inverted matrices which do not contain any cross-terms. Consequently, the standard deviations obtained can be, and, in the present case, obviously are (at least for C-F bondlengths), considerable underestimates.

A careful examination of bondlengths (Table 4.5) shows that the distances from a carbon atom in the benzene ring to a fluorine of the trifluoromethyl group substituted at that position range from 2.30 Å (C4-F11) to 2.43 Å (C4-F12) and fluorine-fluorine contacts, within trifluoromethyl groups, from 2.04 Å (F2-F3) to 2.17 Å (F13-F14). It is quickly apparent that the spread of these values is nowhere near as large as for the C-F bonds within a trifluoromethyl group. Consequently it is extremely probable that the most inaccurately located atoms are not the fluorine atoms, but are the six central carbon atoms of the trifluoromethyl groups. This conclusion appears to be valid since:-

(i) thecarbon atoms of the trifluoromethyl groups at no time appeared as really satisfactory peaks on Fourier syntheses.

(ii) carbon atom positions can be calculated which give far more satisfactory tetrahedra for the trifluoromethyl groups.

Unfortunately, any attempt to use these positions in a block-diagonal least-squares refinement procedure results in the carbon atoms shifting back to the old positions.

(iii) the estimated standard deviations for these carbon atoms are large i.e. up to 0.04 Å (see Table 4.3a) even as calculated from the block-diagonal matrix.

4.6. Thermal Vibrations and Crystal Packing

A careful study of the root mean square amplitudes of vibration and direction cosines of the ellipsoids of vibration for the fluorine atoms (Table 4.10) indicates that each of the six trifluoromethyl groups is undergoing large librational motions. The recognition of these rigid body vibrations is one of the few methods (apart from broad line fluorine magnetic resonance) which is able to indicate whether the large temperature factors of the fluorine atoms results from some large thermal motion or from lattice disorder. Similar librational modes for trifluoromethyl groups have been recognized in the structures of $(P(CF_3))_5$ (Spencer and Lipscomb, 1961), $(CF_3)_4C_5O\ Co(C_5H_5)$ (Gerloch and Mason, 1964) and $(CF_3)_4C_5O\ Fe(CO)_3$ (Bailey, Gerloch and Mason, 1964).

Although the methyl groups in hexamethylbenzene are known to be freely rotating at room temperature (Pauling, 1930) and the van der Waals radii of hydrogen and fluorine are very close (1.20 Å and 1.35 Å respectively; Pauling, 1960), it has been suggested (Harris, Harder and Sausen, 1960) that hexakis(trifluoromethyl)benzene

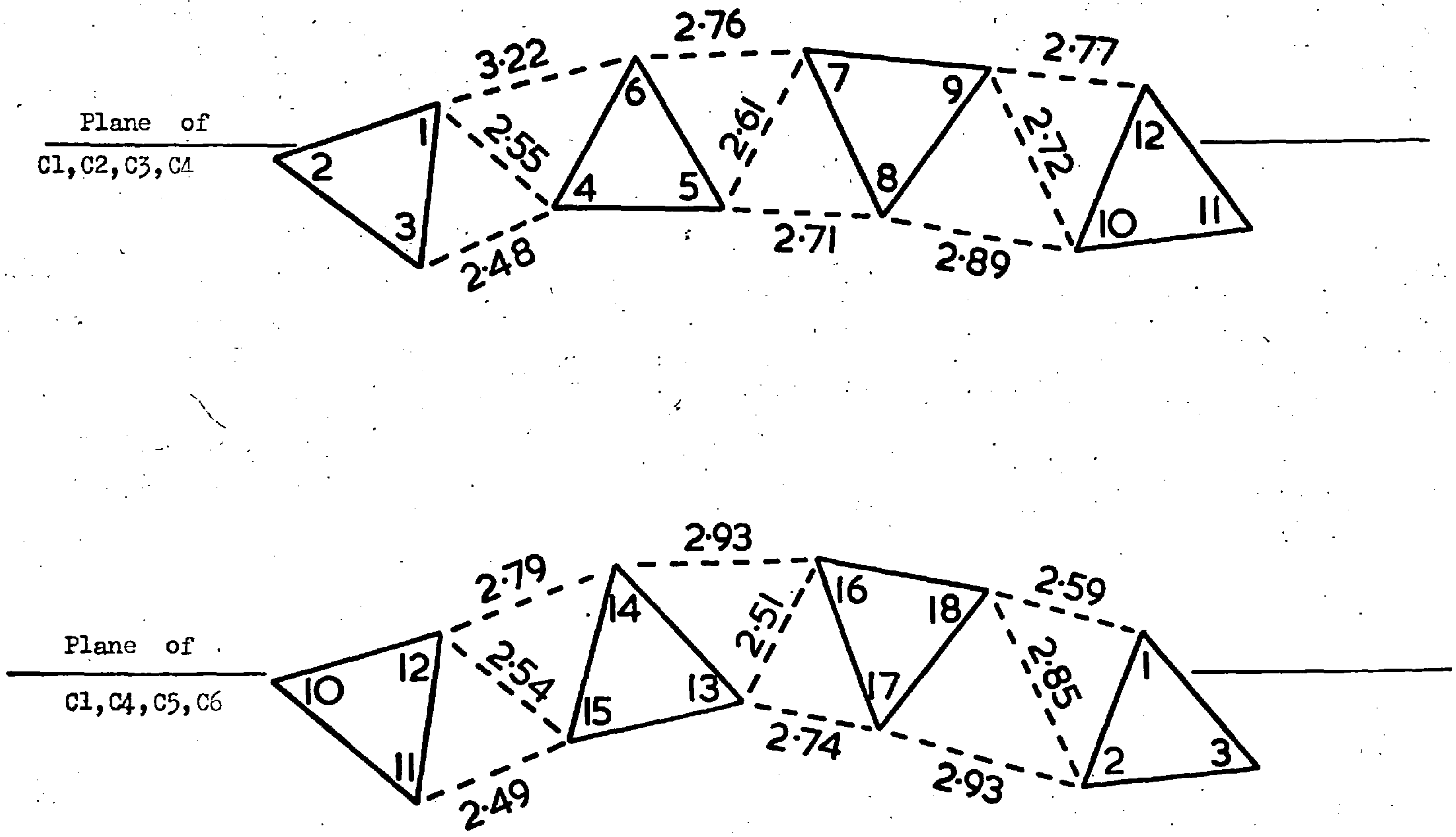


Figure 4.4
Intramolecular Contacts between Neighbouring Trifluoromethyl Groups.

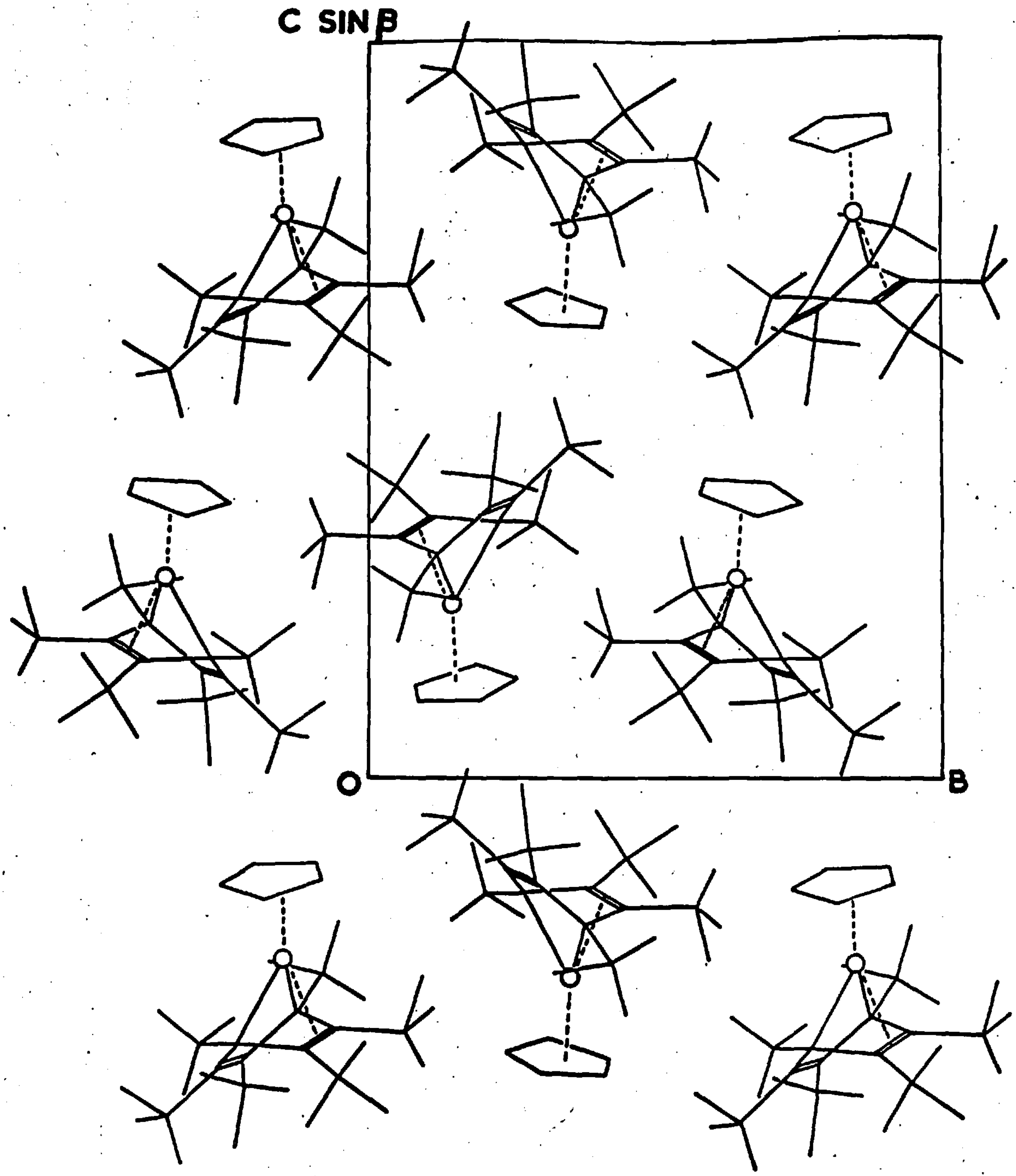


Figure 4.5
π-$C_5H_5Rh(CF_3)_6C_6$ - Packing Diagram (Down 'a').

must be planar, due to the steric interaction of neighbouring trifluoromethyl groups. It must be emphasized that, if the suggestion is correct, the energetically most favoured distortion would be that with alternate trifluoromethyl groups bent above and below the plane of the ring; a dihedral form, as in the present rhodium complex, has few advantages without stabilization by a transition metal, since the resonance energy in the ring will be considerably lowered and the fluorine-fluorine contacts not appreciably relieved.

In π-$C_5H_5Rh(CF_3)_6C_6$, the orientation of each of the six trifluoromethyl groups is best described in terms of the planes formed by the three fluorine atoms. The direction cosines of the normals to the six planes are:-

F1, F2, F3	0.8063,	-0.2247,	-0.5386
F4, F5, F6	0.1042,	-0.9935,	-0.0449
F7, F8, F9	-0.7273,	-0.5098,	0.4595
F10, F11, F12	-0.8398,	0.5386,	-0.0678
F13, F14, F15	0.0952,	-0.7611,	-0.6417
F16, F17, F18	0.8198,	0.0816,	0.5668

The planes defined by F1, F2, F3 and F10, F11, F12 make angles of -72.5° and -70.2° with the plane formed by C1, C2, C3, C4 (the negative sign indicating that the trifluoromethyl groups are displaced towards, rather than away from, the rhodium atom. The same groups of fluorine atoms make angles of -66.1° and -74.4° with the plane formed by C1, C4, C5, C6 thus demonstrating the tetrahedral environments of C1 and C4. The remaining four trifluoromethyl groups are not all strictly perpendicular to their respective planes in the benzene ring, the angles between F_3 groups and the benzene ring being:- +89.1 (F4, F5, F6); +79.8° (F7, F8, F9); +88.4 (F13, F14, F15); +74.1° (F16, F17, F18). It is thus apparent that there is, in fact, a considerable amount of steric interaction between adjacent CF_3 groups. The general pattern of these contacts is illustrated in Figure 4.4. The van der Waals radius for fluorine results in the expected equilibrium fluorine-fluorine distance being 2.70 Å. That several contacts between adjacent trifluoromethyl groups are less than this value, taken with the large (i.e. up to 0.7 Å) r.m.s. amplitudes of vibration of some fluorine atoms, indicates that there is some likelihood of coupled oscillations around the benzene ring.

Hydrogen atom positions have been calculated for the π-cyclopentadienyl ring on the basis of uniform C-H bondlengths of 1.080 Å and an orientation defined by the bisector of the carbon-carbon bond opposite the carbon with which the hydrogen atom is associated. (see Table 4.7). A complete list of intermolecular contacts under 3.5 Å is collected in Table 4.9, including those involving the (calculated) hydrogen atoms. There are no unusually close contacts, the shortest being a fluorine-fluorine contact of 2.74 Å and a fluorine-hydrogen contact of 2.58 Å (both of which are simply the sum of the van der Waals radii of the atoms concerned). A projection, down a, of the molecular packing, is shown in Figure 5.5. The vibration ellipsoids (Table 4.10) show some evidence for a librational mode of the π-cyclopentadienyl ring as well as the previously discussed trifluoromethyl-group librations.

TABLE 4.1

π-$C_5H_5Rh(CF_3)_6C_6$: Progress of Refinement

Cycle	Condition of refinement	R(%)	$\Sigma\omega\Delta^2$
	1622 planes : unit weights		
1	Rh atom only	49.3	2.00×10^9
2	Rh.$C_6(CF_3)_4$ only	37.0	1.75×10^9
3	All atoms in calculation	30.4	8.02×10^8
4	All atoms, isotropic refinement	22.4	4.19×10^8
5	All atoms, anisotropic refinement	18.9	2.60×10^8
6	π-C_5H_5 removed from calculation	18.9	3.93×10^8
7	All atoms, anisotropic refinement	15.2	1.65×10^8
8		13.2	1.13×10^8
9		11.6	8.96×10^7
	2128 planes : unit weights		
10	All atoms, anisotropic refinement	13.3	1.79×10^8
11		12.4	1.34×10^8
12		11.9	1.13×10^8
13	As above, zones carefully rescaled	12.8	1.14×10^8
14		12.3	1.06×10^8
15		11.7	9.86×10^7
16		11.3	9.29×10^7
17		10.9	8.53×10^7
18		10.8	8.35×10^7
19		10.7	8.27×10^7
	2128 planes : reciprocal weights		
20	All atoms, isotropic refinement	11.1	1.22×10^7
21		12.2	1.22×10^7
22		12.6	1.21×10^7

TABLE 4.1 (continued)

Cycle	Condition of refinement	R(%)	$\Sigma\omega\Delta^2$
	Isotropic refinement:reciprocal weights		
23	All atoms in calculation	19.4	4.10×10^8
24		17.6	2.83×10^8
25		16.5	2.49×10^8
26		16.4	2.37×10^8
	Isotropic refinement : "logical" weights		
27	All atoms in calculation	16.4	1.73×10^8
28		18.5	4.49×10^8
29		18.9	2.58×10^8
	Anisotropic refinement:"logical" weights		
30	All atoms in; π-C_5H_5 not refined	12.0	8.68×10^7
31		11.3	7.47×10^7
32		11.1	7.10×10^7
	Extinguished planes removed; 2119 planes; anisotropic refinement		
33	All atoms in, all refined	9.81	5.74×10^7
34		9.77	5.70×10^7
35		9.64	5.53×10^7
36		9.60	5.52×10^7

TABLE 4.2.

Observed and Calculated Structure Factors for π-$C_5H_5Rh(CF_3)_6C_6$

pp. 113-119.

Planes are arranged in blocks of constant h and k; the three columns show ℓ, 50 F_{obs}, 50 F_{calc}.

• 0	0	
2	-9287	-9007
6	-3762	-4284
8	4055	4441
10	-3868	-3950
12	1884	1921
14	-2060	-1790
16	1618	1234
18	-1141	-891
20	598	408
• 0	1	
2	6168	6195
4	4038	4486
5	293	322
6	-773	-759
7	-1325	-1540
8	899	1141
9	1749	1907
10	-2924	-2987
11	-1014	-1063
12	933	1120
13	712	703
14	-1784	-1824
15	-981	-998
16	1341	1226
17	925	806
18	-1130	-907
19	-778	-579
20	679	470
21	477	349
22	-722	-470
• 0	2	
0	-4208	-3903
1	-9774	-9572
2	-1836	-1517
3	7517	7363
5	-3237	-3527
6	730	824
7	5495	5816
8	-3157	-3500
9	-5539	-5569
11	2151	2524
12	-795	-769
13	-2315	-2283
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• 7	3	
-19	-365	-266
-17	696	753
-15	-882	-926
-13	1484	1659
-12	876	1102
-11	-2763	-2508
-10	-593	-583
-9	1940	2020
-8	820	629
-7	-2595	-2490
-6	-988	-1063
-5	2646	2290
-4	1527	1343
-3	-3049	-2833
-2	-1182	-1007
-2	2786	2741
0	1315	1324
1	-1817	-1420
2	-971	-1032
3	2239	1979
4	589	879
5	-2691	-2523
6	-715	-818
7	1622	1684
8	386	308
9	-1006	-976
11	755	607
13	-758	-592
15	554	433
• 7	4	
-20	-904	-786
-18	813	810
-16	-918	-874
-15	759	697
-14	882	843
-12	-1275	-1079
-10	1397	1131
-8	-1549	-1321
-6	1021	905
-4	-783	-706
-3	-728	-479
3	638	623
4	713	751
6	-924	-772
10	-586	-471
• 8	0	
-16	734	559
-14	-1160	-1314
-12	1739	1737
-10	-459	-757
-8	724	1066
-6	-1841	-2178
-4	2951	3458
-2	-2971	-2772
0	1216	1468
2	-1667	-2063
4	1671	1383
6	-1120	-1200
8	954	1005
10	-855	-874
• 8	1	
-22	571	366
-21	371	477
-20	-566	-612
-19	-503	-374
-18	1007	938
-17	490	417
-16	-381	-556

-15	-922	-923
-14	744	968
-13	521	708
-12	-1848	-1838
-11	-1533	-1529
-10	1603	1756
-9	1085	1126
-8	-511	-404
-7	-629	-699
-4	-642	-464
-2	1295	1301
0	-544	-366
2	-676	-696
• 8	2	
-17	747	751
-15	-614	-618
-13	1404	1453
-11	-1787	-1821
-9	1248	1072
-7	-1311	-1282
-6	1029	784
-5	2161	2026
-4	-1286	-1207
-3	-2905	-2787
-2	569	718
-1	1913	2039
1	-2164	-2256
2	485	505
3	2155	2161
4	-495	-558
5	-1489	-1540
7	1184	1156
9	-715	-846
11	669	807
13	-634	-539
• 8	3	
-23	504	277
-21	-669	-556
-20	-379	-302
-19	881	710
-17	-991	-891
-16	-501	-661
-15	1156	1163
-14	595	658
-13	-1275	-1242
-11	1903	1833
-10	580	631
-9	-1200	-1217
-8	-1114	-1265
-7	477	271
-6	936	969
-4	693	545
-3	702	451
0	-327	-237
9	-566	-314
11	646	531
13	-632	-537
• 8	4	
-16	-457	-722
-14	447	646
-13	-441	-458
-12	-818	-805
-11	486	513
-10	1605	1517
-9	-483	-752
-8	-1539	-1613
-7	1240	1212
-6	1094	887
-5	-1711	-1569
-4	-1580	-1568
-3	800	668
-2	2722	2684
-1	-1380	-1103
0	-2217	-2098
1	1264	1260
2	1840	1875
3	-431	-610
4	-1597	-1453
5	573	705
6	1131	1049
7	-586	-640
8	-838	-921
10	912	656

11	-384	-324
12	-604	-419
14	495	360
• 9	0	
-22	535	410
-20	-678	-626
-18	488	457
-16	-595	-614
-14	1130	1082
-12	-1639	-1541
-10	861	742
-8	670	669
-6	583	399
0	-683	-630
• 9	1	
-17	537	464
-16	-551	-556
-15	-244	-416
-14	985	878
-13	539	379
-12	-931	-973
-11	-536	-540
-10	535	382
-8	-1247	-1346
-7	-817	-816
-6	1531	1621
-5	1460	1398
-4	-1260	-1323
-3	-1605	-1501
-2	2004	2052
-1	1452	1374
0	-1622	-1694
1	-888	-948
2	1054	1142
3	757	849
4	-1023	-897
5	-751	-840
6	880	806
7	672	624
8	-930	-789
9	-734	-578
10	598	604
11	437	387
12	-388	-323
• 9	2	
-21	-620	-504
-19	608	514
-17	-651	-522
-15	1063	912
-13	-786	-628
-12	533	591
-11	897	827
-9	-1074	-950
-7	665	395
-6	-859	-797
11	468	439
• 9	3	
-17	-372	-415
-15	508	535
-13	-579	-621
-12	-679	-691
-11	1260	1352
-10	714	727
-9	-1543	-1643
-8	-322	-190
-7	1471	1490
-6	726	719
-5	-1399	-1406
-4	-1169	-1009
-3	1608	1620
-2	968	782
-1	-1848	-1879
0	-621	-524
1	1399	1338
2	350	404
3	-1274	-1158
5	1058	1055
6	568	518
7	-805	-735
9	761	720
11	-523	499
12	-381	-176
13	462	324

• 9	4•	
-18	-627	-611
-16	929	939
-14	-744	-506
-13	640	534
-12	638	242
-10	-971	-993
-8	738	870
-7	-704	-627
-6	-647	-715
-5	654	520
• 10	0	
-16	-551	-641
-14	592	682
-12	-940	-1028
-10	963	1320
-8	-1129	-1349
-6	1210	1422
-4	-1633	-1940
-2	1338	1406
0	-884	-919
2	917	1014
4	-857	-1052
6	1121	1135
• 10	1	
-22	-549	-419
-21	-559	-366
-20	563	484
-19	563	455
-18	-563	-464
-17	-355	-334
-16	687	686
-15	683	651
-14	-786	-727
-12	838	704
-10	-874	-728
-9	-631	-610
-8	875	871
-7	353	250
-6	-353	-502
-5	-501	-417
-3	563	598
• 10	2	
-15	560	621
-13	-597	-634
-11	1238	1467
-9	-1173	-1104
-7	1151	1219
-5	-1528	-1570
-3	1307	1304
-1	-1109	-1058
0	579	527
1	993	1028
3	-624	-941
5	943	974
7	-917	-928
9	563	514
• 10	3	
-23	-402	-254
-21	397	422
-19	-675	-673
-17	665	639
-15	-812	-883
-14	-377	-232
-13	805	643
-11	-649	-623
-9	891	898
-8	535	391
-7	-612	-587
-6	-541	-221
-5	421	614
-1	-559	-217
• 10	4	
-10	-628	-798
-8	1082	1079
-7	-636	-546
-6	-1192	-1077
-5	566	736
-4	1455	1333
-3	-576	-474
-2	-1132	-1057
-1	787	672
0	1023	820
1	-679	-707
2	-1089	-1022
3	425	408
4	1101	801
6	-544	-623
8	541	569
10	-526	-400
• 11	0	
-18	-543	-438
-16	417	448
-14	-472	-580
-12	476	641
-10	-638	-740
-8	476	568
-6	-579	-624
-2	-322	-194
• 11	1	
-13	-395	-242
-12	638	489
-11	562	408
-10	-687	-553
-9	-562	-382
-8	754	777
-7	688	623
-6	-755	-866
-5	-502	-613
-4	642	749
-3	562	606
-2	-684	-761
-1	-497	-471
0	388	446
1	384	425
2	-535	-668
3	-520	-625
4	935	962
5	577	587
6	-520	-551
7	-327	-352
• 11	2	
-21	712	408
-19	-714	-513
-17	502	296
-15	-501	-544
-13	707	543
-11	-707	-643
-9	502	508
-7	-355	-450
-5	508	444
• 11	3	
-15	-391	-327
-13	388	431
-11	-628	-560
-9	678	744
-7	-966	-1037
-5	976	1076
-3	-861	-1003
-1	571	670
0	573	504
1	-702	-622
3	865	887
5	-751	-696
7	539	374
• 11	4	
-12	-771	-584
-10	658	527
-6	588	335
• 12	0	
-12	443	519
-10	-506	-590
-8	669	641
-6	-828	-1106
-4	650	859
-2	-453	-407
0	857	717
• 12	2	
-17	353	317
-15	-504	-583
-13	451	411
-11	-453	-479
-9	577	568
-7	-717	-697
-5	920	865
-3	-504	-616
-1	702	616
1	-684	-766
3	562	620
• 12	3	
-19	399	218
-17	-399	-185
-15	563	427
-13	-853	-647
-11	692	495
-3	443	229
• 12	4	
-10	533	464
-8	-536	-305
-6	688	290
-4	-859	-682
-2	925	789
0	-748	-525
2	741	456
4	-419	-462
6	508	389

Table 4.3. π-$C_5H_5Rh(CF_3)_6C_6$: Atomic Co-ordinates.

RH1	0.25082	0.14485	0.24061
C1	0.49510	0.11856	0.31180
C2	0.39537	0.04917	0.33593
C3	0.29429	0.10418	0.36338
C4	0.31048	0.22384	0.35503
C5	0.47362	0.26111	0.39145
C6	0.57062	0.20761	0.37123
C7	0.57906	0.07580	0.26111
C8	0.41209	-0.07329	0.33731
C9	0.19743	0.05197	0.39987
C10	0.18006	0.28954	0.35624
C11	0.52423	0.35048	0.45742
C12	0.74274	0.21808	0.41604
C13	0.20925	0.19375	0.11464
C14	0.16732	0.08768	0.11028
C15	0.04447	0.08275	0.13549
C16	0.01421	0.18881	0.15525
C17	0.11809	0.25127	0.14015
F1	0.68994	0.00672	0.29701
F2	0.66063	0.16116	0.24943
F3	0.49888	0.04792	0.18908
F4	0.44201	-0.09907	0.26485
F5	0.27439	-0.11774	0.31008
F6	0.50867	-0.10904	0.39178
F7	0.29842	-0.03694	0.45026
F8	0.08077	0.00107	0.35239
F9	0.18192	0.10168	0.45699
F10	0.03791	0.22713	0.32188
F11	0.15041	0.36900	0.30901
F12	0.18516	0.31820	0.42940
F13	0.63470	0.40462	0.46300
F14	0.50609	0.32419	0.52210
F15	0.39945	0.43134	0.42071
F16	0.77264	0.22992	0.50375
F17	0.80563	0.29088	0.39922
F18	0.81722	0.13075	0.42363

Table 4.3a. π-$C_5H_5Rh(CF_3)_6C_6$;

Estimated Standard Deviations.

Atom	σ(X) Å	σ(Y) Å	σ(Z) Å
RH1	0.0012	0.0013	0.0010
C1	0.015	0.014	0.013
C2	0.016	0.017	0.014
C3	0.014	0.015	0.013
C4	0.015	0.015	0.014
C5	0.016	0.014	0.014
C6	0.014	0.016	0.013
C7	0.023	0.032	0.021
C8	0.027	0.019	0.026
C9	0.026	0.026	0.021
C10	0.025	0.025	0.020
C11	0.023	0.026	0.022
C12	0.017	0.023	0.022
C13	0.023	0.026	0.017
C14	0.022	0.024	0.018
C15	0.022	0.024	0.019
C16	0.019	0.031	0.019
C17	0.025	0.022	0.018
F1	0.012	0.013	0.014
F2	0.022	0.020	0.024
F3	0.015	0.020	0.014
F4	0.018	0.015	0.019
F5	0.015	0.011	0.014
F6	0.018	0.012	0.017
F7	0.020	0.019	0.016
F8	0.013	0.018	0.013
F9	0.015	0.016	0.015
F10	0.011	0.022	0.017
F11	0.019	0.016	0.015
F12	0.013	0.013	0.011
F13	0.015	0.013	0.012
F14	0.017	0.012	0.010
F15	0.023	0.012	0.019
F16	0.018	0.016	0.014
F17	0.012	0.018	0.018
F18	0.011	0.016	0.015

Table 4.4. π-$C_5H_5Rh(CF_3)_6C_6$: Anisotropic Thermal Parameters.

The Temperature Factor (T) is described by the equation :-

$$T = 2^{-(b_{11} + b_{22} + b_{33} + b_{23} + b_{13} + b_{12})}$$

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
RH1	0.01652	0.00869	0.00527	0.00045	0.00416	−0.00145
C1	0.02023	0.00613	0.00522	−0.00002	0.00962	−0.00043
C2	0.01751	0.00809	0.00551	−0.00037	−0.00099	0.00233
C3	0.01460	0.00767	0.00472	0.00207	0.00273	−0.01100
C4	0.01729	0.00595	0.00584	0.00052	0.00956	0.00874
C5	0.02293	0.00421	0.00576	−0.00301	0.01217	−0.00213
C6	0.01462	0.00810	0.00540	0.00281	0.00496	−0.01294
C7	0.03363	0.03445	0.00893	−0.01052	0.01658	0.02461
C8	0.04734	0.00546	0.01744	−0.00219	0.03417	−0.00698
C9	0.05081	0.02142	0.01017	−0.00817	0.03212	−0.03684
C10	0.04977	0.02113	0.00894	0.01079	0.02314	0.05452
C11	0.03638	0.02512	0.01137	−0.02065	0.02287	−0.00891
C12	0.01481	0.01506	0.01362	0.00557	0.00677	0.01580
C13	0.03826	0.02233	0.00559	0.00188	0.00197	−0.00048
C14	0.03166	0.01863	0.00700	−0.00244	−0.00434	0.01428
C15	0.03337	0.01695	0.00821	0.00249	−0.01579	−0.02494
C16	0.02168	0.03907	0.00668	0.00657	−0.00146	0.00852
C17	0.04407	0.01325	0.00693	0.00407	0.00098	0.01720
F1	0.03114	0.01728	0.01621	0.00287	0.02585	0.03063
F2	0.10239	0.03544	0.03697	0.04327	0.11343	0.09383
F3	0.04234	0.04434	0.01323	−0.02259	0.01666	0.03286
F4	0.05687	0.01655	0.02393	−0.01815	0.02045	0.00437
F5	0.04626	0.00830	0.01645	−0.00133	0.01822	−0.01248
F6	0.06109	0.00930	0.01873	0.00677	−0.02546	0.00874
F7	0.08057	0.03577	0.01316	0.02234	0.01299	−0.05758
F8	0.03835	0.03502	0.01275	−0.00227	0.01732	−0.05857
F9	0.05200	0.02534	0.01746	−0.01031	0.04724	−0.01559
F10	0.01914	0.05244	0.01978	−0.03291	0.01166	0.02462
F11	0.08241	0.02464	0.01432	0.01111	0.03998	0.06029
F12	0.04273	0.01845	0.01054	−0.00094	0.02838	0.01837
F13	0.05627	0.01517	0.01101	−0.00463	0.01382	−0.03348
F14	0.08481	0.01495	0.00690	−0.00808	0.03088	−0.02825
F15	0.11278	0.00748	0.02462	0.00170	0.07793	0.01284
F16	0.06877	0.02434	0.01214	0.01205	−0.03227	−0.04794
F17	0.01958	0.03358	0.02561	0.03879	0.00905	−0.01998
F18	0.02073	0.02615	0.01764	0.01399	0.01210	0.01213

TABLE 4.5

π-$C_5H_5Rh(CF_3)_6C_6$: Intramolecular Bondlengths and Contacts

(i) Rhodium-carbon distances

Contact	Å	e.s.d.(Å)	Contact	Å	e.s.d.(Å)
Rh - C1	2.150	0.018	Rh - C13	2.195	0.020
Rh - C2	2.064	0.018	Rh - C14	2.232	0.022
Rh - C3	2.109	0.014	Rh - C15	2.207	0.027
Rh - C4	2.119	0.015	Rh - C16	2.189	0.025
Rh - C5	3.010	0.018	Rh - C17	2.166	0.025
Rh - C6	3.052	0.018			

(ii) Bondlengths in the benzene ring

Bond	Å	e.s.d.(Å)	Bond	Å	e.s.d.(Å)
C1 - C2	1.477	0.020	C4 - C5	1.481	0.025
C2 - C3	1.424	0.019	C5 - C6	1.306	0.019
C3 - C4	1.528	0.021	C6 - C1	1.501	0.023

(iii) Bondlengths in the π-cyclopentadienyl ring

Bond	Å	e.s.d.(Å)	Bond	Å	e.s.d.(Å)
C13 - C14	1.386	0.035	C16 - C17	1.372	0.032
C14 - C15	1.414	0.027	C17 - C13	1.344	0.030
C15 - C16	1.440	0.038			

TABLE 4.5 (continued)

(iv) Benzene-trifluoromethyl group : carbon-carbon distances

Bond	Å	e.s.d.(Å)	Bond	Å	e.s.d.(Å)
C1 - C7	1.529	0.024	C4 - C10	1.495	0.029
C2 - C8	1.549	0.025	C5 - C11	1.550	0.031
C3 - C9	1.482	0.025	C6 - C12	1.492	0.028

(v) Carbon-fluorine distances within trifluoromethyl groups

Bond	Å	e.s.d.(Å)	Bond	Å	e.s.d.(Å)
C7 - F1	1.307	0.034	C10 - F10	1.455	0.033
C7 - F2	1.390	0.035	C10 - F11	1.260	0.030
C7 - F3	1.236	0.033	C10 - F12	1.332	0.024
C8 - F4	1.467	0.030	C11 - F13	1.218	0.029
C8 - F5	1.312	0.033	C11 - F14	1.276	0.024
C8 - F6	1.112	0.039	C11 - F15	1.488	0.035
C9 - F7	1.501	0.036	C12 - F16	1.472	0.028
C9 - F8	1.251	0.035	C12 - F17	1.198	0.026
C9 - F9	1.253	0.026	C12 - F18	1.283	0.027

TABLE 4.5 (continued)

(vi) Benzene-trifluoromethyl group : carbon-fluorine distances

Atoms	Å	e.s.d.(Å)	Atoms	Å	e.s.d.(Å)
C1 - F1	2.423	0.019	C4 - F10	2.398	0.021
C1 - F2	2.332	0.023	C4 - F11	2.296	0.025
C1 - F3	2.372	0.020	C4 - F12	2.427	0.017
C2 - F4	2.397	0.022	C5 - F13	2.364	0.022
C2 - F5	2.345	0.021	C5 - F14	2.351	0.018
C2 - F6	2.284	0.023	C5 - F15	2.380	0.019
C3 - F7	2.344	0.023	C5 - F16	2.350	0.027
C3 - F8	2.343	0.021	C6 - F17	2.320	0.021
C3 - F9	2.323	0.017	C6 - F18	2.334	0.022

(vii) Fluorine-fluorine contacts within a trifluoromethyl group

Contact	Å	e.s.d.(Å)	Contact	Å	e.s.d.(Å)
F1 - F2	2.092	0.025	F10 - F11	2.141	0.026
F2 - F3	2.040	0.031	F11 - F12	2.125	0.020
F3 - F1	2.080	0.025	F12 - F10	2.165	0.025
F4 - F5	2.073	0.021	F13 - F14	2.166	0.017
F5 - F6	2.087	0.029	F14 - F15	2.137	0.025
F6 - F4	2.078	0.029	F15 - F13	2.061	0.031
F7 - F8	2.124	0.030	F16 - F17	2.152	0.022
F8 - F9	2.120	0.024	F17 - F18	2.056	0.024
F9 - F7	2.095	0.025	F18 - F16	2.067	0.020

TABLE 4.6.

π-$C_5H_5Rh(CF_3)_6C_6$: Intramolecular Angles (with e.s.d.'s)

	Angle°	e.s.d.°
C1 - Rh - C4	73.6	0.6
C6 - C1 - C2	114.3	1.1
C1 - C2 - C3	114.6	1.4
C2 - C3 - C4	109.7	1.1
C3 - C4 - C5	113.5	1.4
C4 - C5 - C6	116.3	1.4
C5 - C6 - C1	113.3	1.5
C17 - C13 - C14	109.2	1.9
C13 - C14 - C15	106.2	1.9
C14 - C15 - C16	108.2	2.0
C15 - C16 - C17	104.5	1.7
C16 - C17 - C13	111.9	2.2
C2 - C1 - C7	121.2	1.6
C6 - C1 - C7	117.8	1.6
Rh - C1 - C2	66.4	1.0
Rh - C1 - C6	112.2	1.0
Rh - C1 - C7	113.9	1.4
C1 - C2 - C8	121.3	1.4
C3 - C2 - C8	123.9	1.4
C2 - C3 - C9	124.3	1.6
C4 - C3 - C9	125.9	1.4
C3 - C4 - C10	115.3	1.4
C5 - C4 - C10	122.5	1.6

TABLE 4.6 (continued)

	Angle°	e.s.d.°
Rh - C4 - C3	68.5	0.8
Rh - C4 - C5	112.3	0.8
Rh - C4 - C10	112.6	1.5
C4 - C5 - C11	119.8	1.4
C6 - C5 - C11	123.5	1.8
C5 - C6 - C12	122.3	1.4
C1 - C6 - C12	123.1	1.7
F1 - C7 - F2	101.8	2.0
F2 - C7 - F3	101.8	2.1
F3 - C7 - F1	109.7	2.4
C1 - C7 - F1	117.2	1.9
C1 - C7 - F2	106.0	2.2
C1 - C7 - F3	117.7	2.1
F4 - C8 - F5	96.3	2.1
F5 - C8 - F6	118.5	1.9
F6 - C8 - F4	106.5	2.1
C2 - C8 - F4	105.2	1.6
C2 - C8 - F5	109.8	2.0
C2 - C8 - F6	117.3	2.4
F7 - C9 - F8	100.6	2.1
F8 - C9 - F9	115.6	2.1
F9 - C9 - F7	98.6	2.0
C3 - C9 - F7	103.6	1.9
C3 - C9 - F8	117.8	1.9
C3 - C9 - F9	116.0	2.2

TABLE 4.6 (continued)

	Angle°	e.s.d.°
F10 - C10 - F11	103.9	2.4
F11 - C10 - F12	110.1	2.0
F12 - C10 - F10	101.8	1.6
C4 - C10 - F10	108.7	1.8
C4 - C10 - F11	112.6	1.7
C4 - C10 - F12	118.2	2.3
F13 - C11 - F14	120.5	2.6
F14 - C11 - F15	101.0	1.7
F15 - C11 - F13	98.7	2.0
C5 - C11 - F13	116.8	1.6
C5 - C11 - F14	112.3	1.9
C5 - C11 - F15	103.1	2.1
F16 - C12 - F17	107.0	2.1
F17 - C12 - F18	111.9	1.5
F18 - C12 - F16	97.0	1.9
C6 - C12 - F16	104.9	1.3
C6 - C12 - F17	118.8	2.2
C6 - C12 - F18	114.3	1.9

TABLE 4.7

π-$C_5H_5Rh(CF_3)_6C_6$: Calculated Hydrogen Positions

	X	Y	Z
H13	0.30066	0.22319	0.09903
H14	0.21785	0.02156	0.09159
H15	-0.01602	0.01181	0.13959
H16	-0.07225	0.21270	0.17655
H17	0.12433	0.33629	0.14899

TABLE 4.8

π-$C_5H_5Rh(CF_3)_6C_6$: Inter-annular Intramolecular Contacts (to 3.8 Å)

Atom	Contact	Dist. Å	Atom	Contact	Dist. Å
C1	- C13	3.55	C10	- H17	3.55
	- C14	3.65	F2	- H13	3.43
	- H13	3.69	F3	- C13	3.10
C2	- C14	3.70		- C14	2.90
	- C15	3.75		- H13	2.90
C3	- C15	3.75		- H14	2.52
	- C16	3.69	F4	- C14	3.72
C4	- C16	3.51		- H14	3.29
	- C17	3.49	F5	- H15	3.53
	- H16	3.69	F8	- H15	3.50
	- H17	3.62	F10	- C16	2.92
C7	- C13	3.69		- C17	3.63
	- C14	3.70		- H16	2.36
	- H13	3.51		- H17	3.76
	- H14	3.56	F11	- C16	3.37
C10	- C16	3.49		- C17	3.25
	- C17	3.67		- H16	3.12
	- H16	3.42		- H17	2.78

TABLE 4.9

π-C_5H_5.Rh$(CF_3)_6C_6$: Intermolecular Contacts less than 3.5 Å

Atom	Contact	Distance (Å)
C6	F4 (1-x, ½+y, ½-z)	3.40
C10	H15 (-x, ½+y, ½-z)	3.22
C11	F15 (1-x, 1-y, 1-z)	3.38
C12	F7 (1-x, -y, 1-z)	3.43
C13	F12 (x, ½-y, -½+z)	3.21
C14	F12 (x, ½-y, -½+z)	3.50
C16	F16 (-1+x, ½-y, -½+z)	2.90
C17	F16 (-1+x, ½-y, -½+z)	3.16
F1	F8 (1+x, y, z)	3.41
	F11 (1-x, -½+y, ½-z)	3.35
	H17 (1-x, -½+y, ½-z)	2.69
F2	F4 (1-x, ½+y, ½-z)	3.15
	F5 (1-x, ½+y, ½-z)	3.13
	F10 (1+x, y, z)	3.36
	H16 (1+x, y, z)	3.36
F3	F13 (1-x, -½+y, ½-z)	3.05
	F14 (x, ½-y, -½+z)	3.40
	F15 (1-x, -½+y, ½-z)	2.91
F4	F17 (1-x, -½+y, ½-z)	3.20
	H13 (1-x, -½+y, ½-z)	3.45
F5	F10 (-x, -½+y, ½-z)	3.50
	H16 (-x, -½+y, ½-z)	2.94
F6	F7 (1-x, -y, 1-z)	3.21
	F9 (1-x, -y, 1-z)	3.04

TABLE 4.9 (continued)

Atom	Contact	Distance (Å)
F6	F14 (1-x, -y, 1-z)	3.14
	H13 (1-x, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)	2.74
F7	F16 (1-x, -y, 1-z)	2.74
	F18 (1-x, -y, 1-z)	3.11
F8	F11 (-x, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)	3.25
	H17 (-x, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)	2.84
F9	F18 (-1+x, y, z)	3.27
	H13 (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)	3.18
F10	F17 (-1+x, y, z)	3.15
F11	H15 (-x, $\frac{1}{2}+y$, $\frac{1}{2}-z$)	2.58
F12	F17 (-1+x, y, z)	3.43
	H13 (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)	2.79
	H14 (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)	3.43
	H15 (-x, $\frac{1}{2}+y$, $\frac{1}{2}-z$)	2.89
F13	F15 (1-x, 1-y, 1-z)	3.03
	H14 (1-x, $\frac{1}{2}+y$, $\frac{1}{2}-z$)	2.49
F14	F15 (1-x, 1-y, 1-z)	3.25
	H13 (x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)	2.87
F15	F15 (1-x, 1-y, 1-z)	3.17
	H15 (-x, $\frac{1}{2}+y$, $\frac{1}{2}-z$)	3.48
F16	H16 (1+x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)	2.89
	H17 (1+x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)	3.36
F17	H14 (1-x, $\frac{1}{2}+y$, $\frac{1}{2}-z$)	2.92

TABLE 4.10

π-$C_5H_5Rh(CF_3)_6C_6$: Root mean square amplitudes and direction cosines of the Atomic Vibration Ellipsoids

Atom	$\sqrt{\overline{u^2}}_{max.}$ (Å) (d.c.'s of major axis)	$\sqrt{\overline{u^2}}_{med.}$ (Å) (d.c.'s of median axis)	$\sqrt{\overline{u^2}}_{min.}$ (Å) (d.c.'s of minor axis)
Rh	0.250 (0.745,-0.268,-0.611)	0.218 (0.117, 0.954,-0.276)	0.197 (-0.657,-0.135,-0.742)
C1	0.23 (0.804,-0.039, 0.593)	0.21 (-0.592, 0.042, 0.805)	0.18 (-0.056,-0.998, 0.010)
C2	0.30 (0.811, 0.122,-0.572)	0.21 (-0.005, 0.979, 0.203)	0.18 (-0.585, 0.162,-0.795)
C3	0.28 (0.701,-0.603,-0.381)	0.19 (-0.189, 0.359,-0.914)	0.14 (-0.688,-0.713,-0.138)
C4	0.24 (0.675, 0.536, 0.506)	0.23 (-0.414,-0.292, 0.862)	0.14 (-0.610, 0.712,-0.025)
C5	0.25 (0.644,-0.194, 0.740)	0.22 (0.759, 0.282,-0.587)	0.14 (0.095,-0.940,-0.329)
C6	0.29 (0.647,-0.657,-0.388)	0.21 (-0.280, 0.269,-0.922)	0.11 (0.710, 0.704,-0.009)
C7	0.48 (0.403, 0.892,-0.205)	0.30 (0.527,-0.042, 0.849)	0.19 (0.749,-0.450,-0.487)
C8	0.41 (0.273,-0.078, 0.959)	0.31 (0.951,-0.129,-0.281)	0.17 (-0.145,-0.989,-0.039)
C9	0.45 (0.618,-0.655, 0.435)	0.27 (-0.025,-0.570,-0.821)	0.20 (-0.786,-0.496, 0.368)
C10	0.48 (0.665, 0.687, 0.293)	0.26 (-0.339,-0.073, 0.938)	0.14 (0.665,-0.723, 0.184)
C11	0.45 (-0.032,-0.788, 0.615)	0.30 (0.907, 0.236, 0.349)	0.19 (-0.420, 0.569, 0.707)

TABLE 4.10 (continued)

Atom	$\sqrt{u^2}_{\mathrm{max.}}$ (Å) (d.c.'s of major axis)	$\sqrt{u^2}_{\mathrm{med.}}$ (Å) (d.c.'s of median axis)	$\sqrt{u^2}_{\mathrm{min.}}$ (Å) (d.c.'s of minor axis)
C12	0.38 (0.369,-0.156,-0.916)	0.31 (0.473, 0.880, 0.041)	0.15 (-0.800, 0.449,-0.399)
C13	0.37 (0.836,-0.501,-0.225)	0.35 (0.504, 0.862,-0.049)	0.21 (-0.219, 0.073,-0.973)
C14	0.41 (0.789, 0.492,-0.367)	0.29 (0.367, 0.858, 0.360)	0.20 (-0.492, 0.149,-0.858)
C15	0.48 (0.818,-0.375,-0.436)	0.28 (0.133, 0.861,-0.491)	0.15 (-0.560,-0.344,-0.754)
C16	0.47 (0.018, 0.990, 0.142)	0.33 (0.831, 0.064,-0.552)	0.19 (-0.555, 0.128,-0.822)
C17	0.41 (0.940, 0.270,-0.209)	0.29 (-0.073, 0.756, 0.650)	0.20 (-0.334, 0.596,-0.731)
F1	0.39 (0.324, 0.472, 0.820)	0.37 (0.525, 0.632,-0.571)	0.14 (-0.787, 0.615,-0.043)
F2	0.73 (0.423, 0.510, 0.749)	0.32 (-0.237,-0.735, 0.635)	0.13 (-0.874, 0.446, 0.190)
F3	0.58 (0.429, 0.837,-0.340)	0.33 (0.572, 0.040, 0.819)	0.21 (-0.700, 0.546, 0.461)
F4	0.53 (0.491, 0.375,-0.786)	0.38 (0.851,-0.014, 0.524)	0.25 (-0.186, 0.927, 0.326)
F5	0.41 (0.580-0.085,-0.810)	0.35 (0.770,-0.267, 0.580)	0.20 (-0.265,-0.960,-0.090)
F6	0.63 (0.830,-0.022,-0.559)	0.30 (-0.478,-0.548,-0.687)	0.19 (-0.291, 0.836,-0.465)
F7	0.63 (0.714,-0.657,-0.241)	0.37 (-0.522,-0.271,-0.809)	0.18 (-0.466,-0.704, 0.536)

TABLE 4.10 (continued)

Atom	$\sqrt{u^2}_{\text{max.}}$ (Å) (d.c.'s of major axis)	$\sqrt{u^2}_{\text{med.}}$ (Å) (d.c.'s of median axis)	$\sqrt{u^2}_{\text{min.}}$ (Å) (d.c.'s of minor axis)
F8	0.53 (0.565,-0.825, 0.016)	0.34 (0.099, 0.048,-0.994)	0.14 (0.819, 0.563, 0.109)
F9	0.46 (0.382,-0.502, 0.776)	0.34 (-0.256,-0.864,-0.433)	0.23 (0.888,-0.034,-0.458)
F10	0.64 (0.329, 0.805,-0.494)	0.33 (0.136, 0.478, 0.868)	0.17 (-0.935, 0.353,-0.048)
F11	0.55 (0.734, 0.583, 0.348)	0.33 (-0.294,-0.189, 0.937)	0.23 (-0.612, 0.790,-0.033)
F12	0.38 (0.662, 0.628, 0.410)	0.32 (0.075,-0.600, 0.796)	0.20 (0.746,-0.496,-0.444)
F13	0.45 (0.878,-0.479,-0.003)	0.33 (0.149, 0.279,-0.949)	0.21 (-0.455,-0.832,-0.316)
F14	0.49 (0.891,-0.319, 0.323)	0.27 (-0.416,-0.858, 0.300)	0.20 (0.181,-0.402,-0.898)
F15	0.57 (0.683, 0.074, 0.727)	0.34 (0.708, 0.177,-0.684)	0.19 (0.179,-0.982,-0.069)
F16	0.66 (0.834,-0.383,-0.398)	0.30 (0.200, 0.881,-0.430)	0.20 (-0.515,-0.279,-0.811)
F17	0.64 (0.386,-0.617,-0.685)	0.29 (-0.409, 0.551,-0.727)	0.15 (-0.827,-0.561, 0.040)
F18	0.46 (0.222,-0.586,-0.780)	0.34 (0.440, 0.774,-0.456)	0.22 (0.870,-0.242, 0.429)

CHAPTER V

THE CRYSTAL AND MOLECULAR STRUCTURE OF OCTAFLUOROCYCLOHEXA-1,3-DIENEIRON TRICARBONYL

5.1. Introduction

Although butadiene iron tricarbonyl had been known since 1930 (Reihlen et al.), it was not until 1958 that Hallam and Pauson prepared the analogous cyclohexadiene complex $C_6H_8Fe(CO)_3$. Since that time complexes of cyclohexadiene with vanadium, chromium, molybdenum, manganese, ruthenium, cobalt and silver have been isolated (Fischer and Werner, 1963).

Hoehn, Pratt, Watterson and Wilkinson (1961) found that the perfluoro-cyclohexa-1,3-diene complex, $C_6F_8Fe(CO)_3$ could be isolated from the reaction of tri-iron-dodecacarbonyl with either octafluorocyclohexa-1,3- or -1,4-diene, the latter case providing an example of fluorine migration.

The crystal structure of octafluorocyclohexa-1,3-dieneiron tricarbonyl was investigated in an attempt to elucidate the nature of the metal → conjugated diene bonding.

5.2. Experimental

Octafluorocyclohexa-1,3-dieneiron tricarbonyl is completely air-stable in the crystalline state, but is reported (Hoehn et al., 1961) to be rather unstable in solution, even under anaerobic conditions. Since the compound is extremely volatile, a small sample completely disappearing in twenty minutes at room temperature, it was found convenient to grow crystals by slow sublimation. Pale yellow orthorhombic needles, with well-developed 100 and 001 faces were obtained by this method on storing a sample of the compound (sealed under atmospheric pressure) at -5° C for some four-six weeks. Crystals were mounted along their needle axis (b) and prevented from subliming by a protective coating of polymer (polyvinyl formal from a 2% solution in dichloroethane). A number of crystals having dimensions averaging 0.15 x 0.15 x 0.30 mm. were used during the analysis.

Equi-inclination Weissenberg data were collected for the $\{h0\ell\}$, $\{h1\ell\}$, $\{h2\ell\}$ and $\{h3\ell\}$ zones and precession data for the $\{hk0\}$, $\{hk1\}$, $\{hk2\}$, $\{0k\ell\}$ and $\{2h,k,h\}$ zones.

Since molybdenum radiation, $\bar{\lambda}(K_{\alpha}) = 0.7107$ Å, was used for all data collection, no correction was made for absorption.

5.3. Unit-cell and Spacegroup

The unit cell parameters, from a study of high angle precession and Weissenberg data, were found to be:-

$$a = 13.49 \pm 0.02 \text{ Å}$$

$$b = 6.92 \pm 0.01 \text{ Å}$$

$$c = 11.89 \pm 0.02 \text{ Å}$$

The observed density, by flotation in Rohrbach's solution is $\rho(\text{obs}) = 2.15 \pm 0.02$ g. cm.$^{-3}$ which is in agreement with the calculated density $\rho(\text{calc}) = 2.179$ g. cm.$^{-3}$ for $Z = 4$, $M = 364$

and V = 1110 Å^3.

The absences h0ℓ for h = 2n + 1 and 0kℓ for ℓ = 2n + 1 allow the alternative spacegroups Pcam (no. 57) or Pca2$_1$ (no. 29) depending upon whether or not the possible molecular and crystal mirror-planes coincide.

5.4. Solution of the Phase Problem

The crystal was originally assumed to be in the non-centrosymmetric spacegroup Pca2$_1$ which has the equipoints:-

x,	y,	z
$\frac{1}{2}-x$,	y,	$\frac{1}{2}+z$
$\frac{1}{2}+x$,	$-y$,	z
$-x$,	$-y$,	$\frac{1}{2}+z$

These equipoints lead to the following twelve vectors (m = multiplicity) between iron atoms:-

m = 2	$\frac{1}{2}+2x$,	0 ,	$\frac{1}{2}$
	$\frac{1}{2}-2x$,	0 ,	$\frac{1}{2}$
	$\frac{1}{2}$,	$2y$,	0
	$\frac{1}{2}$,	$-2y$,	0
m = 1	$2x$,	$2y$,	$\frac{1}{2}$
	$-2x$,	$2y$,	$\frac{1}{2}$
	$2x$,	$-2y$,	$\frac{1}{2}$
	$-2x$,	$-2y$,	$\frac{1}{2}$

In the non-centrosymmetric spacegroup $Pca2_1$, the Z-coordinate of the metal is arbitrary. Hence in theory, the two-dimensional Patterson synthesis P(UVO) should locate the heavy atom. This projection will show vectors:-

m = 2	$\frac{1}{2}+2x$,	0
	$\frac{1}{2}-2x$,	0
	$\frac{1}{2}$,	$2y$
	$\frac{1}{2}$,	$-2y$
	$2x$,	$2y$
	$2x$,	$-2y$
	$-2x$,	$2y$
	$-2x$,	$-2y$

A two-dimensional Patterson synthesis, calculated from the 109 reflexions of the hk0 zone showed a set of vectors consistent with a metal position of $x/a = 0.075$, $y/b = 0.115$. However, structure factor calculations using this position failed to refine below 0.60 (indicating that the metal position was highly suspect). Two sections (the Harker sections, $z/c = 0$ and $z/c = \frac{1}{2}$) of a three-dimensional Patterson synthesis immediately indicated that the correct iron position was in fact, $x/a = 0.021$, $y/b = 0.20$.

The incorrect location of the metal by two-dimensional methods was due to the "piling-up" of iron-fluorine, and other light-atom vectors, resulting in misleadingly high peaks and is a very good example of the dangers in relying solely on two-dimensional Patterson syntheses in compounds containing several light atoms.

5.5. Refinement of Structure

A structure factor calculation, phased by the iron atom at 0.021, 0.20, 0.00, had a reliability factor of 0.47 which decreased to 0.45 after a single least-squares refinement of positional and thermal parameters. A three-dimensional Fourier synthesis was calculated using as coefficients structure factors phased only by the iron atom. This, for a non-centrosymmetric spacegroup should, in theory, locate the true molecule and also show its equally weighted reflection about the Z-coordinate (here, $Z = 0$) where the metal has been placed. The Fourier synthesis, however, showed only one molecule although there was a strict mirror plane at $Z = 0$. Hence, one half of the molecule is the mirror image of the other half, and the two are related by a strict crystallographic mirror plane. The spacegroup is therefore Pcam and not the pre-assumed $Pca2_1$. The atomic coordinates of all light atoms were determined from the three-dimensional Fourier synthesis and adjusted (by adding $\frac{1}{4}$ to the Z-coordinate) so as to agree with the standard setting for spacegroup Pcam.

Structure factors, phased by all atoms, had an initial reliability factor of 0.199 which reduced smoothly to 0.115 (see Table 5.1) after four cycles of isotropic refinement and to 0.058 after a further six cycles of positional and anisotropic thermal parameter refinement. At this point four planes, which had been observed as only extremely weak reflexions were removed from the refinement and a further five cycles reduced the reliability factor to 0.0569, at which point maximum suggested positional shifts were less than 0.0002 Å (i.e. less than one-fortieth of an estimated standard deviation) and shifts of the anisotropic vibrational parameters were correspondingly small. Final observed and calculated structure factors for the 666 observed planes are shown in Table 5.2., and a composite Fourier, phased by these values, in Figure 5.1. The atomic coordinates are given in Table 5.3. and the vibrational parameters in Table 5.4.

5.6. Discussion of Molecular Structure

As can easily be seen from Figure 5.2., the molecule possesses a strict mirror plane passing through Fe, C5 and O2. Atoms below this mirror plane at $z/c = \frac{1}{4}$ are numbered similarly to their mirror images above the plane but are suffixed by a dash; thus C4' is the mirror image of C4 across $z/c = \frac{1}{4}$.

All bondlengths, important intramolecular contacts and bond-angles are collected in Table 5.5. Estimated standard deviations of the positional parameters were obtained from the diagonal elements of the inverted 3 x 3 matrices used to obtain the final (negligible) shifts. Since the matrix contains no inter-atomic or positional-vibrational cross terms, the calculated values for the e.s.d.'s are questionable but are unlikely to have been underestimated by more than twenty per cent since the actual rate (and ease) of refinement

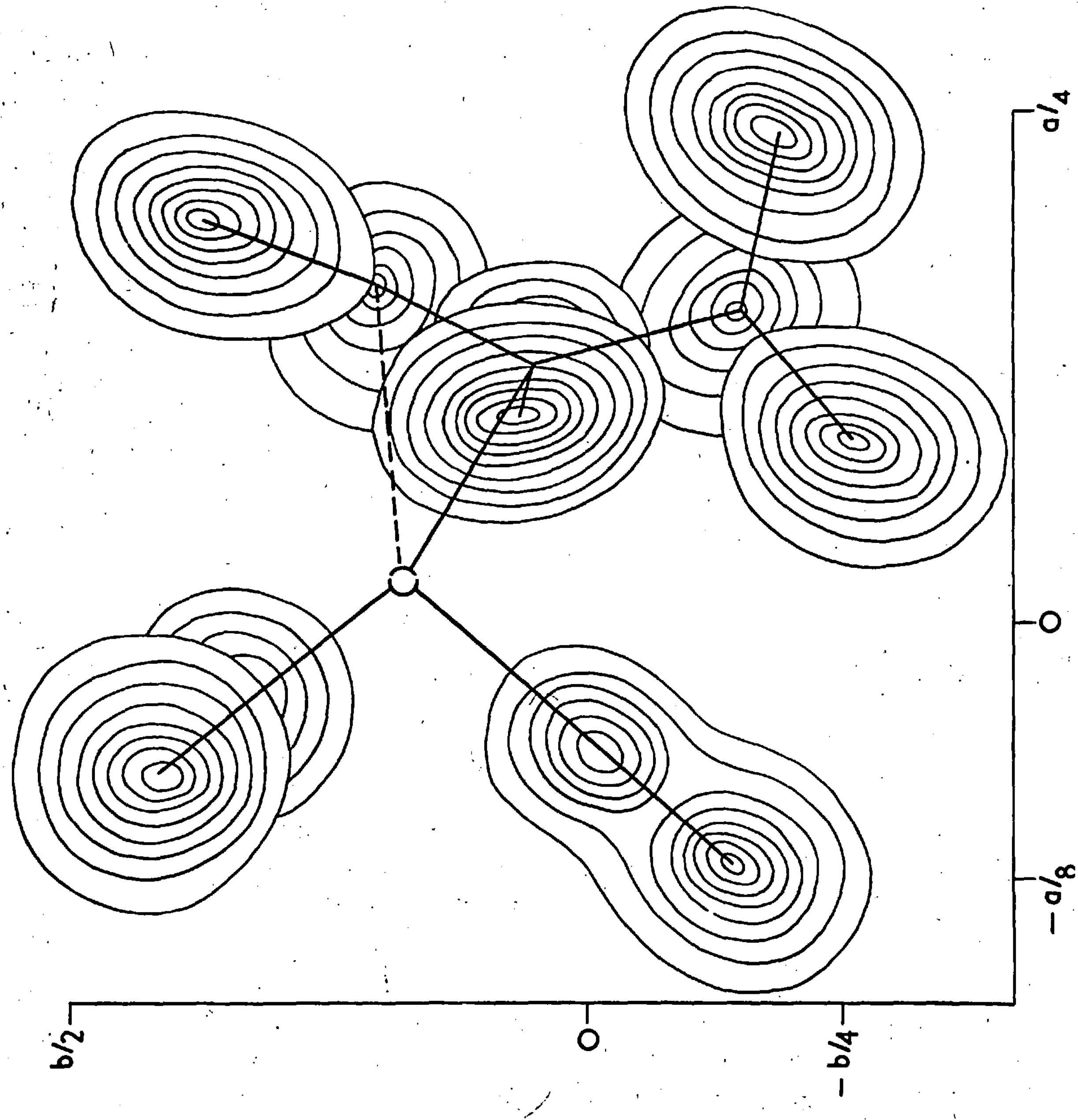

Figure 5.1
$C_6F_8Fe(CO)_3$ - Composite Fourier (Sectioned down 'c').

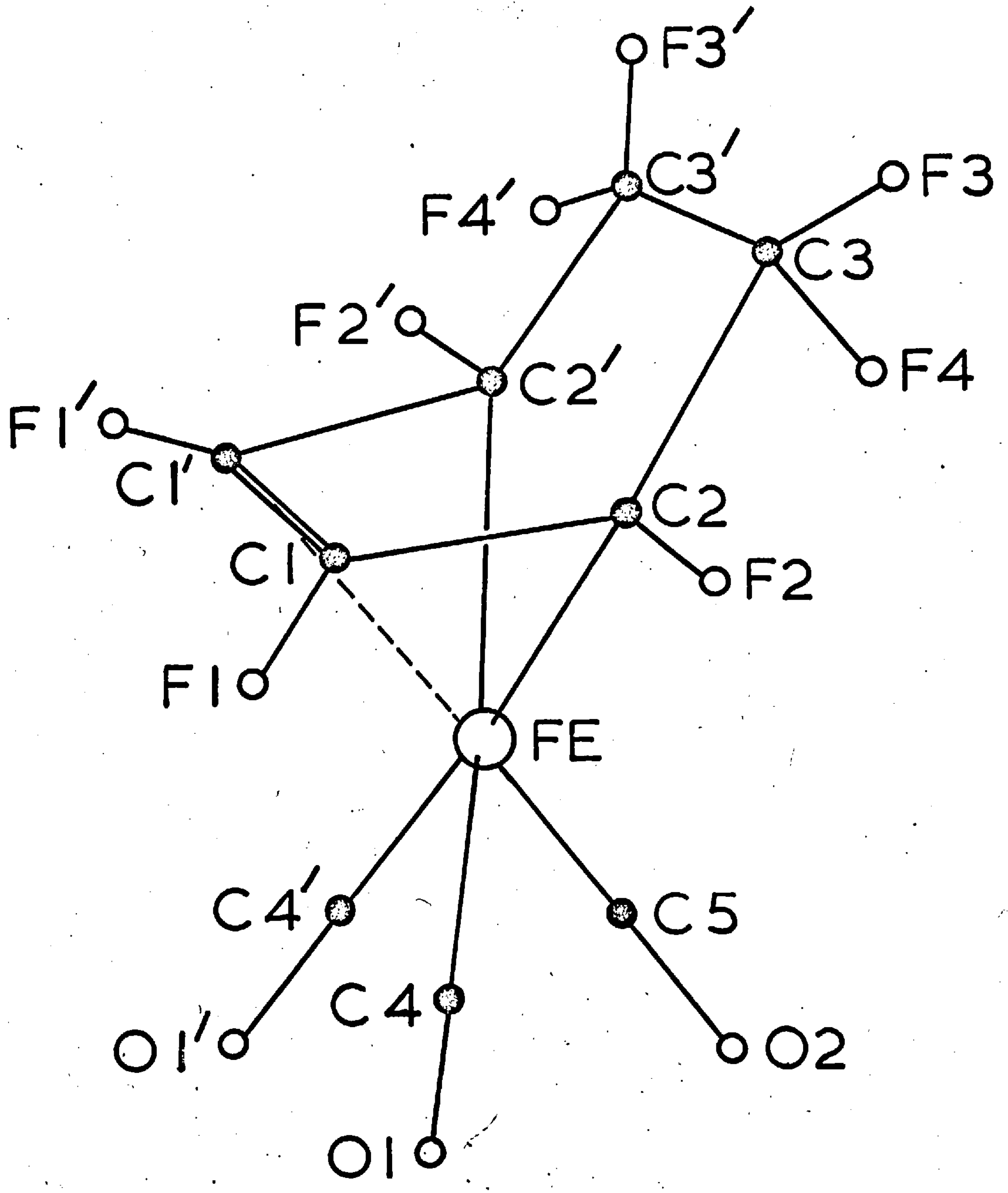

Figure 5.2.

$C_6F_8Fe(CO)_3$ - Numbering of Atoms.

indicates that cross-terms are very small. The low e.s.d.'s of the bondlengths and bond-angles result from there being so few variables (a total of 33 positional, 66 vibrational and one scale parameter) and such a high ratio of observed planes to parameters (6.66 : 1).

The detailed bondlengths and angles in the cyclohexadiene are shown in Figure 5.3. The ligand has strict mirror symmetry with the mirror plane, bisecting the C1 - C1 and C3 - C3' bonds. The plane of the butadiene cosines (d.c.'s) -0.86899, 0.49483, 0.00000; the plane C2'-C3'-C3-C2 has d.c.'s -0.95269, -0.30394, 0.00000; each of the two planes is required to be strictly planar. The saturated part of the molecule is thus bent away from the butadiene portion by an angle of 47.3°. This large distortion from planarity can be explained only by a change in hybridization of the atoms C2 and C2' from the sp^2 valence state in the uncoordinated ligand to an sp^3 valence state in the present complex. This is substantiated by the position of F2 which is 0.107 Å below the butadiene plane (towards the metal) and, consequently, in the position expected for the fourth member of the tetrahedron surrounding C2. Further evidence for localised bonding to C2 and C2' is provided by the unexpectedly short distance of 2.53 Å between these two atoms, and by a careful study of angles in the butadiene portion of the ring. The angles C1'-C1-C2 and C1-C1'-C2' are decreased from the expected 120° to the present value of 114.4° and the angles C1-C2-C3 and C1'-C2'-C3'

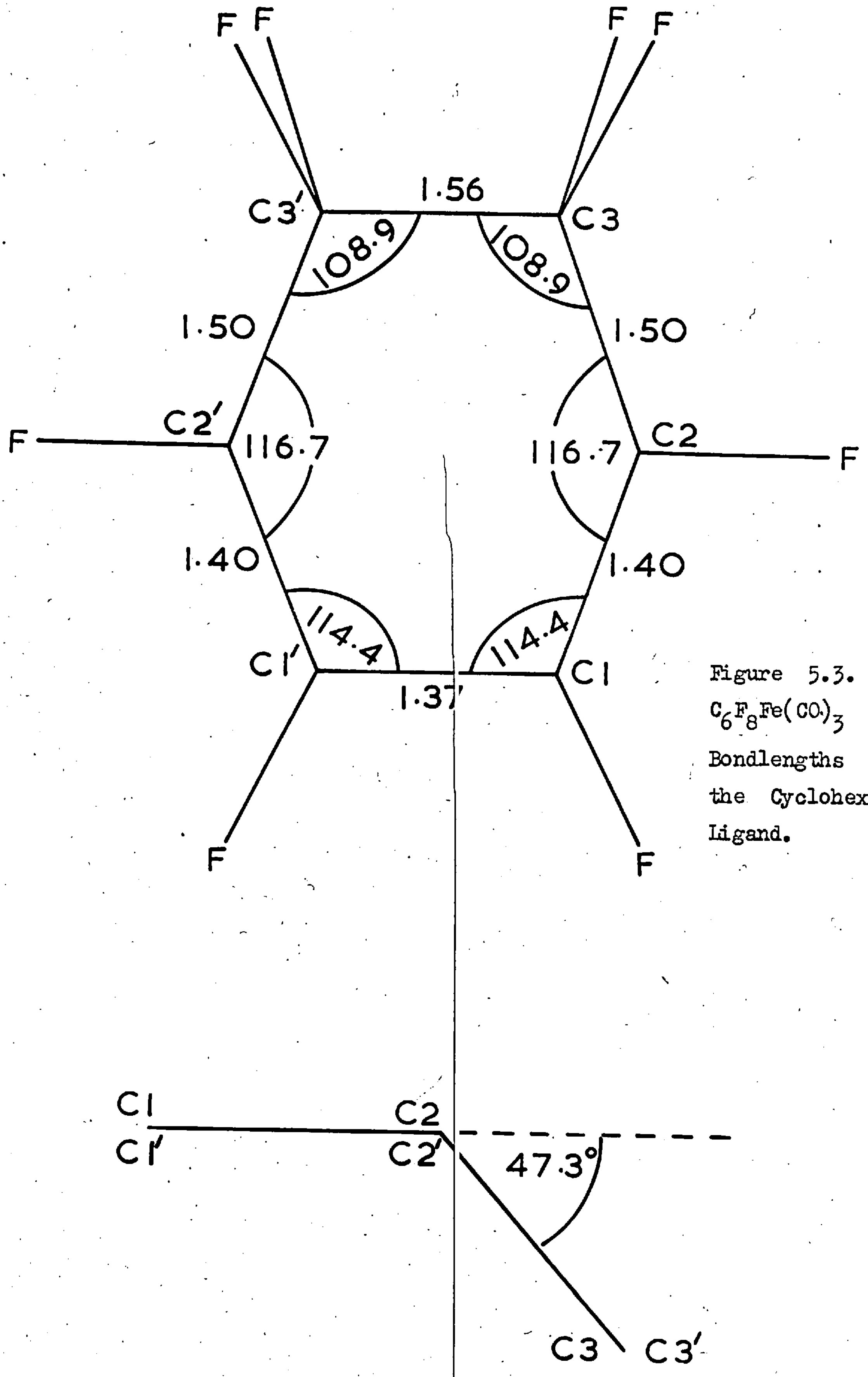

Figure 5.3. $C_6F_8Fe(CO)_3$ - Bondlengths in the Cyclohexadiene Ligand.

increased from the expected tetrahedral angle to a value of 116.7° by the "squeezing together" of atoms C2 and C2'. The very small and statistically insignificant reduction of the angles C2-C3-C3' and C3-C3'-C2 to the present value of 108.9° is in the same sense as the considered distortion.

The butadiene moiety is regarded as bonding to the iron atom by one π- and two σ-bonds. The iron-carbon σ-bonds are of length 1.993 Å and although the Fe-C1 distance is 2.060 Å, the distance of the iron atom from the centre of the π-bond is 1.932 Å. Although the bondlengths in the butadiene system C2'-C1'-C1-C2 are 1.397 Å, 1.374 Å, 1.397 Å, with the central bond only slightly the shorter, the only possible valence-bond structure is that shown in Figure 5.2. However, the observed bondlengths can be explained within the framework of the more sophisticated molecular-orbital treatment (see Chapter 6).

The literature values for carbon-fluorine bondlengths (Interatomic Distances, 1958) show that the value of 1.38_1Å found in monofluoro-compounds is reduced to 1.33_4 Å in a $-CF_2-$ group. This decrease has been explained (Peters, 1963) in terms of charge-transfer from carbon to fluorine. A carbon-fluorine bond adjacent to a double bond is 1.32_5 Å in length (Interatomic Distances, 1958). The distances of 1.33_0Å for C1-F1 and 1.36_2Å for C2-F2 are in good agreement with the above values. However, the values for C3-F3 and C3-F4 are, respectively, 1.36_8Å and 1.33_6Å. The difference between these two values appears to be significant, with the C3-F3 value anomalously large. It is difficult to rationalize this observation, since all close contacts (both inter- and intramolecular) involve F3 rather than F4 and would be expected to shorten, rather than lengthen the C3-F3 bond. It is interesting to note that the smallest angle of the tetrahedron at C3 is that between the two fluorine atoms, and is 106.2°. The close intramolecular contacts of F3 and F3' (2.460 Å) and F4 and F4' (2.458 Å) do not seem to cause any significant distortion in the tetrahedral arrangement about C3, since F3 is 1.075 Å above, and F4 1.087 Å below, the plane formed by the atoms C2, C3, C3' and C2'. The lengthening of C3-C3' from the normal sp^3-sp^3 value of 1.54 Å to the present value of 1.558 Å can be explained in terms of these fluorine-fluorine repulsions acting across the mirror plane at $z/c = \frac{1}{4}$ or in terms of an electronic effect (or both). (Bowen (1954), on electronic grounds, suggested a value of 1.55 - 1.60 Å for the carbon-carbon distance in trifluoroacetamide and Brockway and Schwendeman (see Sutton, 1959) obtained a value of 1.54 ± 0.02 Å from gas phase electron-diffraction studies as against 1.50 ± 0.01 Å for acetamide itself (Kilb et al., 1957). X-ray structural investigations of monofluoroacetamide (Hughes and Small, 1962) and ammonium trifluoroacetate (Cruickshank, Jones and Walker, 1964) show that the value of the sp^2-sp^2 carbon-carbon bond is increased by about 0.03 Å from the value of 1.51 Å now accepted for hydrocarbon compounds).

In simple valence-bond terms, the iron atom is in a formal oxidation state of +2, with a d^6 electronic configuration and the concomitant (distorted) octahedral environment. The carbonyl groups C4-O1 and C4'-O1' trans- to the σ-bonding centres (C2 and C2') make an angle of 89.6° at the central metal atom. The angles C4-Fe-C5 and C4'-Fe-C5 are each 97.8°. This distortion from perfect C_{3v} symmetry is further evidenced by the carbon-carbon and oxygen-oxygen contacts between the three carbonyl groups (C4-C4' = 2.540 Å, C4-C5 = 2.714 Å, C4'-C5 = 2.714 Å; O1-O1' = 4.012 Å, O1-O2 = 4.427 Å, O1' - O2 = 4.427 Å),

A comparison with other conjugated diene complexes containing the tricarbonyl-iron group shows that this distortion is general, that the sense is always the same and that the magnitude is (approximately) constant. In $(CF_3)_4C_5O.Fe(CO)_3$ (Bailey, Gerloch and Mason, 1964) the angles formed at the iron atom by the carbonyl groups are 89.4°, 95.0°, 97.5°; in $C_8H_8Fe(CO)_3$ (Dickens and Lipscomb, 1962) these angles are 92.7°, 100.7°, 100.7° and in $(OC)_3FeC_8H_8Fe(CO)_3$ the two tricarbonyl-iron groups have the angles 90°, 102°, 101° and 94°, 97°, 101°. In each case the small angle is that opposite to the two σ-bonding carbon atoms. That butadiene iron tricarbonyl (Mills and Robinson, 1963) also shows this same sense of distortion, the angles being 93°, 102°, 102°, indicates that the final description of the butadiene-metal bonding in this molecule may well contain contributions from a localized metal-ligand interaction.

A simple explanation of these distortions can be made. The distortion of the $Fe(CO)_3$ group from C_{3v} symmetry must be due to the nature of the group attached to the "other side" of the iron atom i.e., in the present case, the cyclohexadiene ligand. The pattern of the distortions is such that the bond Fe-C5 (which is trans- to the double-bond C1-C1') has less 'd'-character (the angles C4-Fe-C5 and C4'-Fe-C5 being closer to the sp^3 angle than the angle C4-Fe-C4', which is almost exactly correct for a d^2sp^3 hybrid angle). This can be explained by the d-electrons being preferentially associated with the C1-C1' double-bond and therefore not so available for participation in the metal-carbonyl bond (Fe-C5) trans- to this "electron sink". Although the angular distortions are great, there is no a priori reason why there should be any discernable difference in the metal-carbonyl bondlengths, since the energy requirements for bond-stretching are considerably greater than those for angular distortions. In fact the bond Fe-C5 (1.799 Å) is slightly shorter than Fe-C4 (1.803 Å) but this difference is not statistically significant.

The three carbon atoms of the carbonyl groups form a plane (d.c.'s -0.98846, 0.15150, 0.00000) which makes an angle of 20.95° with the plane of the butadiene moiety C2', C1', C1, C2. The three oxygens form a plane having the direction cosines 0.99044, -0.13792, 0.00000.

5.7. Crystal Packing and Atomic Vibrations

The crystal packing is illustrated by the three orthogonal projections down 'a' (Figure 5.4), down 'b' (Figure 5.5) and down 'c' (Figure 5.6). All intermolecular contacts up to 3.8 Å are collected in Table 5.6. The shortest two contacts are F1 - F4 (2.96 Å) and O1 - F4 (2.97 Å). These are, of course, considerably longer than the equilibrium van der Waals' distances of 2.70 Å (F - F contact) and 2.75 Å (F - O contact). The root mean square amplitudes of vibration, which are collected (along with the direction cosines for the axes of the vibration ellipsoids) in Table 5.7, show that the 'external' atoms of the molecule, i.e. the eight fluorine and three oxygen atoms, are those which are undergoing the largest amplitudes of vibration. This large amplitude of vibration results in "time-instantaneous excursions" of the atoms to their van der Waals' contact positions, and is completely consistent with the extremely high volatility of the complex.

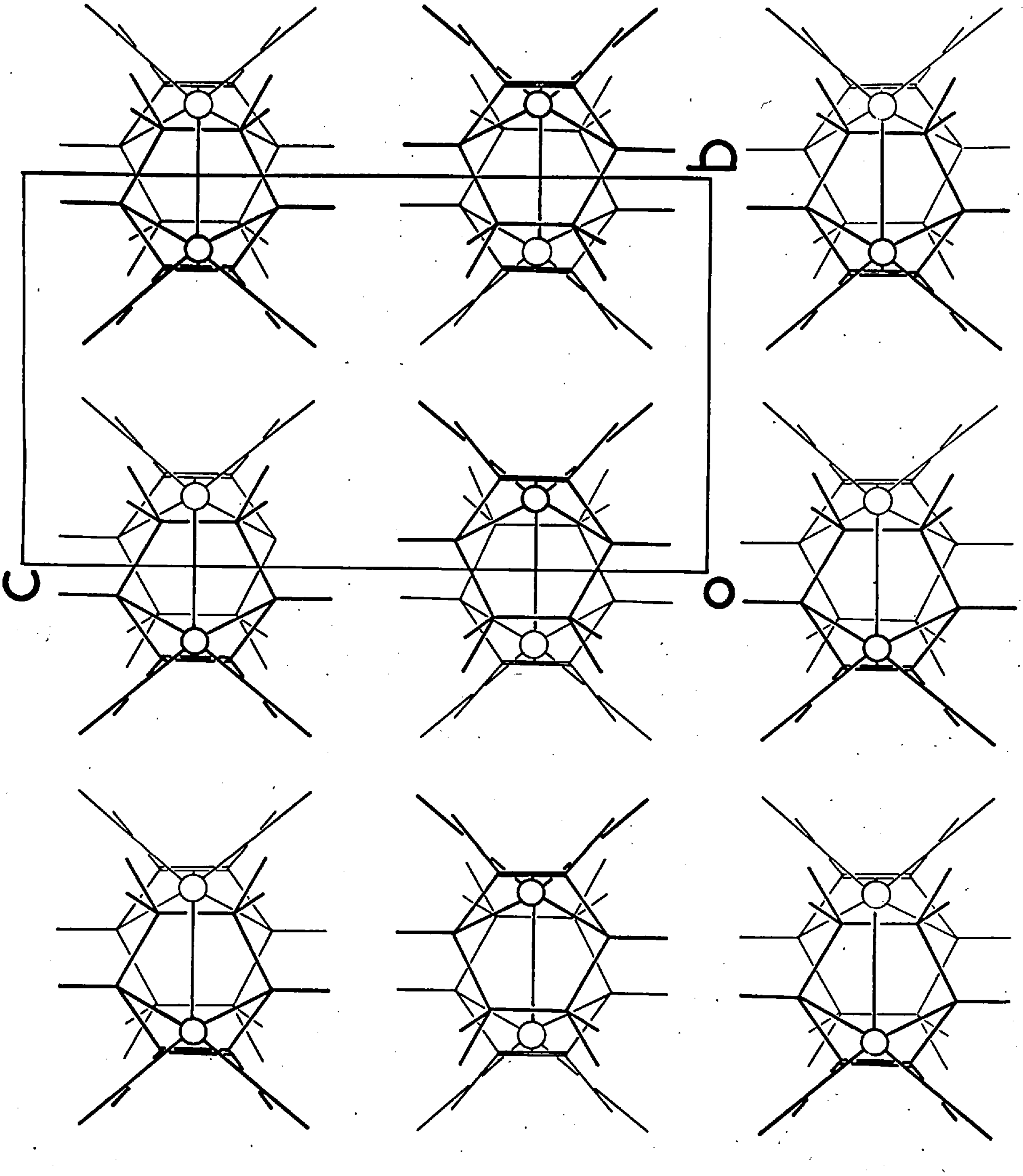

Figure 5.4.
$C_6F_8Fe(CO)_3$ - Packing Diagram (Projection down 'a').

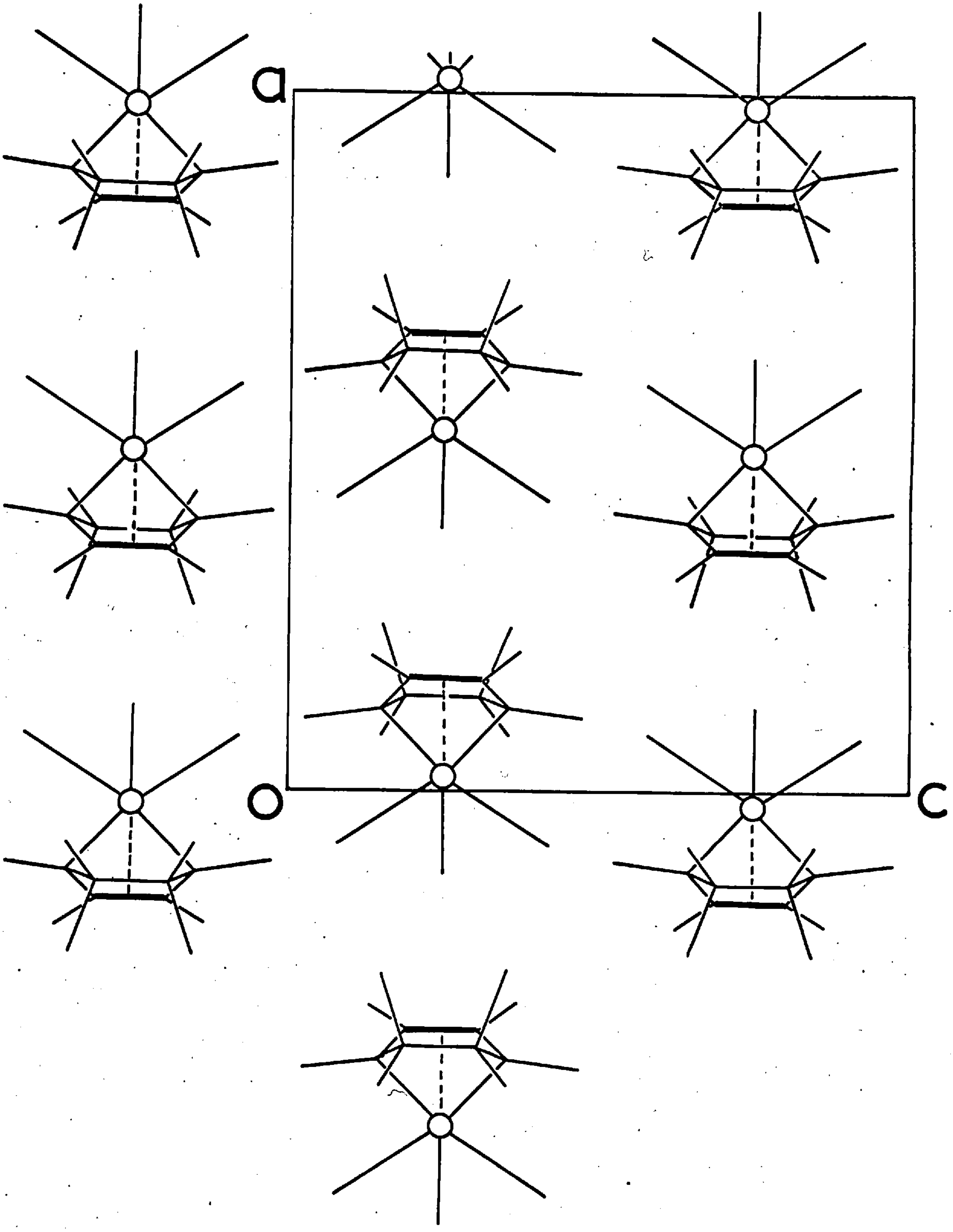

Figure 5.5. - Packing Diagram (Projection down 'b').

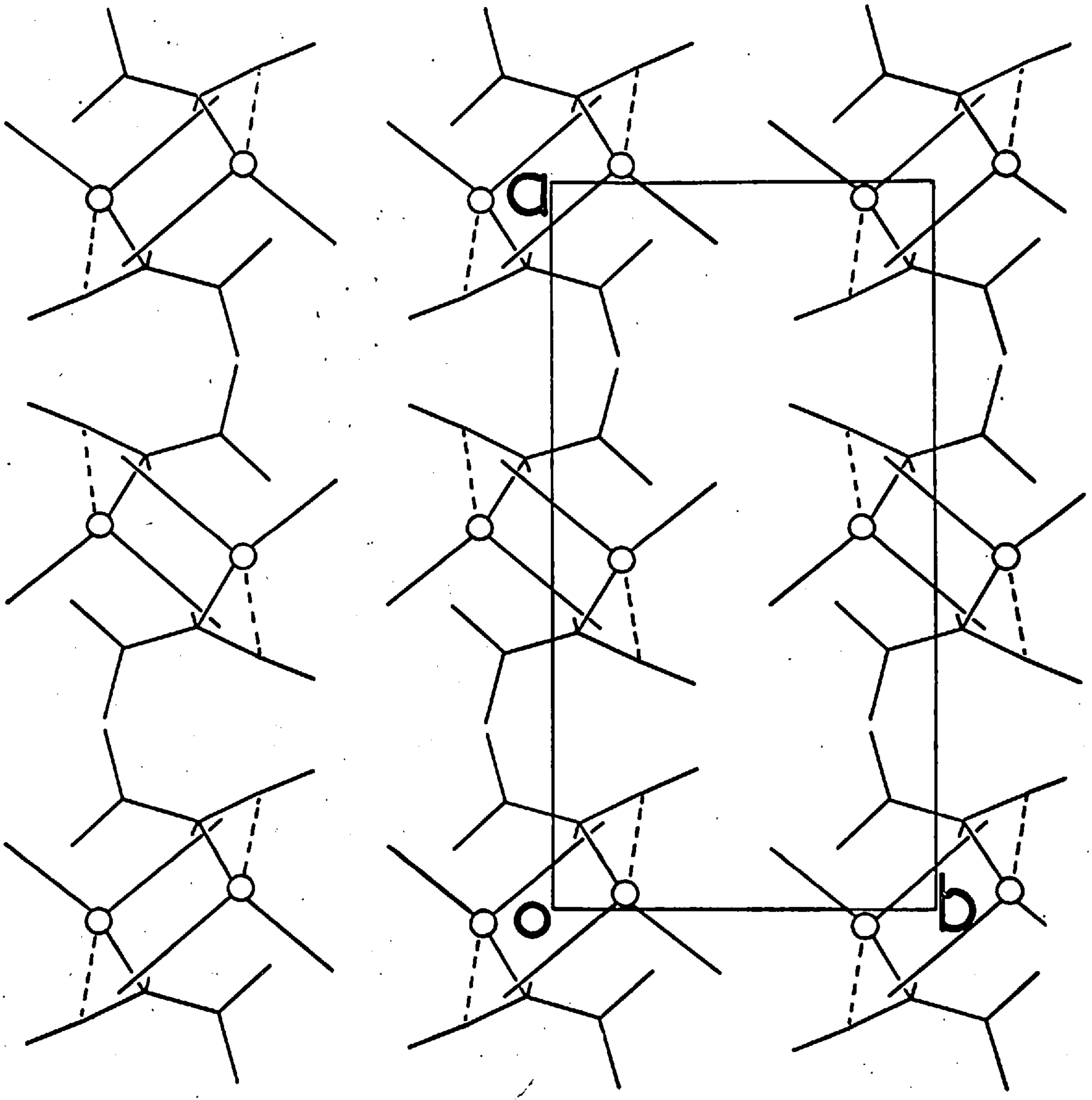

Figure 5.6. Packing Diagram (Projection down 'c').

TABLE 5.1

Progress of refinement : unit weights throughout

Cycle	Maximum suggested shifts (fractional coordinates) Δx	Δy	Δz	R	$\Sigma\omega\Delta^2$
Iron only : wrong position					
1	-	-	-	0.60	2.985×10^9
2	-	-	-	0.62	2.223×10^9
Iron only : correct position					
1	-	-	-	0.47	1.667×10^9
2	-	-	-	0.45	1.468×10^9
All atoms : isotropic thermal parameters					
1	0.00413	0.02240	0.00743	0.199	7.235×10^7
2	0.00279	0.00593	0.00204	0.123	3.083×10^7
3	0.00095	0.00165	0.00104	0.119	2.531×10^7
4	0.00065	0.00056	0.00038	0.118	2.390×10^7
Zones rescaled : isotropic input : anisotropic refinement					
1	0.00048	0.00161	0.00061	0.115	2.083×10^7
Anisotropic refinement					
1	0.00047	0.00142	0.00193	0.0692	8.333×10^6
2	0.00039	0.00059	0.00034	0.0612	6.557×10^6
3	0.00029	0.00056	0.00042	0.0591	6.095×10^6
4	0.00013	0.00022	0.00016	0.0586	5.943×10^6
5	0.00007	0.00019	0.00014	0.0583	5.881×10^6
6	0.00004	0.00008	0.00007	0.0582	5.855×10^6
Four unreliable low intensity planes removed					
1	0.00006	0.00041	0.00033	0.0572	5.586×10^6
2	0.00004	0.00022	0.00009	0.0569	5.548×10^6
3	0.00002	0.00010	0.00006	0.0569	5.534×10^6
4	0.00001	0.00005	0.00002	0.0569	5.529×10^6
5	0.00001	0.00003	0.00001	0.0569	5.527×10^6

TABLE 5.2.

Observed and Calculated Structure Factors for $C_6F_8Fe(CO)_3$

pp. 156-158

Planes are arranged in blocks of constant h and k; the three columns are ℓ, $50|F_{obs}|$, $50\ F_{calc}$.

●	0	0	
2		8464	-3639
4		2192	-2064
8		3086	3153
10		2605	-2545
12		753	799
14		524	-465
16		280	260
●	0	1	
0		6231	5767
2		3302	-3264
4		5097	4917
6		687	657
8		1169	1119
10		1015	-1030
14		410	-443
●	0	2	
0		5233	-5013
2		6358	6223
4		224	185
8		1439	-1350
10		709	712
12		455	-503
14		328	307
●	0	3	
0		3441	-3354
2		3784	3698
4		2845	-2720
6		2016	1836
8		895	-879
10		480	431
12		756	-834
14		475	513
●	0	4	
0		1335	-1300
2		655	-571
4		943	907
6		484	-498
8		297	-285
●	0	5	
0		2425	2355
2		2095	-2103
4		1180	1118
6		1721	-1701
8		1074	984
10		880	-829
12		565	614
14		338	-348
●	0	6	
2		1029	-1040
4		840	832
6		997	-992
8		746	759
10		357	-381
12		237	242
●	0	7	
0		791	-811
2		372	333
8		598	-523
10		350	357
●	0	8	
0		245	-261
2		283	289
4		595	-620
6		601	601
8		451	-450
●	1	1	
1		4224	-4527
2		280	193
3		1730	1719
4		2575	-2585
5		3046	-3363
6		968	1001
7		1774	1843
9		1780	-1780
11		896	909
13		569	-560
14		183	140
●	1	2	
0		1141	1276
1		187	184
2		1844	-1318
3		2603	2690
4		3665	-3508
5		2458	-2326
6		1402	1145
9		1596	-1446
●	1	3	
0		2274	-2358
1		335	-304
2		631	-662
3		4384	-4620
4		1159	1118
5		1828	1694
6		1079	-1014
7		1209	-1151
8		1133	-1080
10		631	657
11		423	-339
●	1	4	
0		1637	-1685
1		2150	2305
2		1092	-1116
●	1	5	
0		414	-404
●	1	6	
0		1177	-1205
1		1883	-2053
●	1	7	
0		370	345
1		1070	-1200
●	1	8	
0		247	278
1		555	529
●	1	9	
1		578	699
●	2	0	
0		4779	4278
1		6380	-6866
2		2480	-2514
3		1400	-1448
4		4910	5381
5		2886	2947
6		3713	-3977
7		2231	-2293
8		1737	1886
9		1419	-1527
10		1472	-1565
11		374	-490
12		911	1044
14		388	-477
●	2	1	
0		778	758
1		2380	-2393
2		1644	-1543
3		3534	-3614
4		2520	2467
5		549	-491
6		903	-891
7		1674	-1521
8		1133	1200
10		539	-546
14		259	-308
●	2	2	
0		1019	-947
1		3547	3547
2		2752	2599
3		809	-851
4		1790	-1747
6		1428	1358
7		1376	-1056
8		1769	-1548
10		1145	1041
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2		1360	1370
3		1197	-1328
4		2620	-2765
6		2906	2844
8		1316	-1273
10		457	451
11		244	-204
12		646	-607
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2		701	-655
●	2	5	
0		776	740
1		297	-280
2		1539	-1486
●	2	5	
0		465	428
1		947	909
2		1078	-1051
●	2	7	
0		442	-449
1		491	550
2		515	505
●	2	8	
0		798	-828
2		674	658
●	3	1	
0		204	-97
1		3401	-3444
2		1298	1128
3		3643	3921
4		3191	-3527
5		2626	-2610
6		709	629
7		2092	2211
8		791	-793
9		1502	-1519
10		472	487
11		1152	1249
13		559	-574
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7		2072	1838
8		1322	-1224
9		603	-544
10		1079	1022
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2		601	-666
4		173	-45
5		546	565
6		1403	-1299
7		1293	-1176
8		712	-600
9		1593	1503
11		489	-393
12		519	419
●	3	4	
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2		2493	-2354
●	3	5	
0		718	730
1		1316	1405
2		447	-471
●	3	6	
0		793	-734
2		392	441
●	3	7	
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2		490	447
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1		398	475
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6		2102	-2098
8		2212	2094
9		1142	-1178
10		1192	-1230
12		748	829
13		294	-434
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3		3132	-3255
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9		539	-582
12		461	460
●	4	2	
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2		1026	957
3		540	-569
4		1550	-1538
5		935	833
6		1550	1264
7		1502	-1417
8		1502	-1418
10		1265	1255
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2		1582	1513
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4		1159	-1307
5		623	539
6		1133	1108
7		1465	-1444
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9		1104	1083
10		1209	1069
11		346	-434
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2		2060	-1934
●	4	6	
0		2043	2117
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7		2126	2071
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12		496	-479
13		381	-394
14		350	398
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3		3260	3337
4		895	-820
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6		1145	952
7		1663	1579
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2		713	701
3		519	487
4		669	725
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6		1486	-1529
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9		691	659
10		598	-521
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12	428	376
13	328	-417
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7	1072	1113
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12	366	425
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5	1502	1491
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7	809	-718
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4	2551	-2637
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6	1065	955
7	1037	-976
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10	691	652
11	691	-694
12	546	-424
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1	1677	-1751
2	987	-1050
3	373	264
• 6	6	
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0	751	-790
2	559	591
3	472	-329
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3	646	-526
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9	656	676
10	777	-847
11	605	646
12	328	302
13	498	-511
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0	4037	3957
1	1252	-1170
2	1948	1933
4	984	-856
5	436	408
7	507	460
8	549	457
10	539	-481
11	350	398
• 8	2	
0	1006	-917
1	754	803
2	1297	1237
3	2142	-2155
4	1243	-1131
5	2055	1951
6	1402	1250
• 8	3	
0	2993	-2986
1	2463	2479
2	1933	1919
3	1316	-1254
4	549	-517
5	846	749
6	546	536
7	546	-558
8	977	-991
9	898	751
10	573	614
• 8	4	
0	667	-748
2	516	520
4	464	-375
• 8	5	
1	924	-1037
2	623	-625
4	694	630
• 8	6	
0	398	440
2	392	-432
• 8	7	
4	405	-340
• 8	8	
0	564	-500
• 9	1	
0	1410	-1389
2	1806	1689
3	660	664
4	2219	-2160
5	1167	-1090
6	1857	1792
7	423	403
8	769	-725
9	613	-640
10	668	641
12	549	-593
• 9	2	
0	1013	-964
1	652	-631
2	1357	1347
4	540	-633
6	1112	973
8	1207	-1299
• 9	3	
0	2044	1954
1	647	-593
2	1253	-1198
3	733	-704
5	881	802
7	946	-893
8	598	590
• 9	4	
0	1365	1503
2	749	-801
• 9	5	
0	1152	-1107
• 9	6	
0	350	-455
2	696	712
• 9	7	
0	352	-331
• 10	0	
0	1445	1300
1	1820	-1852
2	675	679
3	911	886
4	498	563
5	1858	-1740
6	940	-893
7	1132	1188
8	923	999
9	1033	-1056
10	428	-439
11	741	821
13	402	-456
• 10	1	
0	271	-211
1	1083	-1041
2	612	596
3	607	568
4	974	924
9	812	-823
• 10	2	
0	360	362
2	508	567
3	1402	-1349
4	603	-501
5	1111	1025
6	714	893
7	853	-819
• 10	3	
0	438	433
1	1439	1434
3	489	-537
4	993	-950
5	619	534
6	829	766
7	733	-799
8	519	-488
9	598	642
• 10	4	
5	638	-502
• 10	5	
0	436	465
1	1162	-1246
2	429	-388
5	1082	-938
• 10	6	
0	315	-310
1	657	-649
5	295	-298
• 10	7	
0	285	-328
1	411	340
• 10	8	
0	295	-254
1	639	637
• 11	1	
0	3014	-3048
1	899	-662
2	1700	1582
3	461	437
4	921	-930
5	717	-708
6	933	956
8	1157	-1201
10	933	929

• 11	2	
0	1982	−1844
1	1003	−911
2	1352	1262
4	1176	−1164
6	540	405
• 11	3	
0	906	−917
1	375	−362
2	479	−525
3	573	−622
4	753	772
6	753	−754
• 11	4	
0	1030	1094
1	789	846
2	1188	−1244
• 11	5	
0	455	507
2	586	−627
• 11	6	
0	432	−433
2	369	395
• 11	7	
0	401	−391
• 12	0	
0	505	555
1	1278	−1459
2	294	−214
3	990	874
5	1699	−1738
6	248	−267
7	1224	1271
8	428	−398
9	1192	−1205
11	464	482
• 12	1	
1	294	−341
3	588	600
5	818	−831
6	393	348
9	607	−589
• 12	2	
0	748	−710
1	347	388
2	628	595
3	1207	−1047
5	661	877
6	489	−375
7	809	−871
• 12	3	
0	819	−776
3	1079	−1034
4	712	619
5	1079	1036
6	387	−234
7	598	−710
• 12	4	
0	955	962
1	370	−340
• 12	5	
0	333	457
1	797	−963
• 12	6	
1	366	−336
• 12	7	
1	400	380
• 12	8	
1	390	449
• 13	1	
0	1039	−1112
1	667	603
2	1150	1225
3	616	617
4	1421	−1481
5	818	−786
6	933	906
8	549	−535
• 13	2	
0	1115	−1114
2	644	718
4	809	−732
• 13	3	
0	607	576
1	301	345
2	743	−777
6	546	−492
• 13	4	
0	780	814
1	239	344
2	999	−1061
• 13	6	
0	580	−597
2	458	512
• 14	0	
0	393	−351
1	1711	−1790
3	1571	1606
5	837	−922
7	557	546
8	374	−341
9	519	−544
• 14	1	
0	257	−340
1	756	−801
2	362	−322
5	472	−429
7	448	386
• 14	2	
1	1531	1438
2	312	−267
7	436	−406
• 14	3	
1	1095	1173
3	712	−733
5	546	550
7	721	−628
• 14	4	
1	292	−423
• 14	5	
1	586	−682
• 14	6	
1	233	−304
• 15	1	
0	581	−585
1	331	339
2	830	886
3	528	−450
4	762	−724
6	507	545
• 15	3	
0	802	863
2	448	−458
6	423	−271
• 15	4	
0	783	815
2	687	−755
• 15	5	
0	326	254
• 15	6	
2	455	547
• 16	0	
0	428	−384
1	825	−870
2	294	239
3	811	899
5	415	−408
7	605	559
9	415	−441
11	453	351
• 16	2	
0	552	556
1	663	699
2	370	−432
• 16	3	
1	501	491
3	773	−781
5	669	739
• 16	5	
1	397	−340
• 17	1	
0	493	−472
1	327	348
2	433	503
4	423	−421
6	616	578
• 17	4	
1	401	−395
• 18	0	
0	369	−360
1	338	−358
• 18	2	
1	440	450
• 18	3	
1	336	352
• 18	5	
1	316	−323
• 19	1	
0	651	−661
2	437	533
• 21	1	
0	423	−364
• 22	0	
0	476	−425

TABLE 5.3

$C_6F_8Fe(CO)_3$: Atomic coordinates with estimated standard deviations

Atom	x/a	y/b	z/c	σ(X) (Å)	σ(Y) (Å)	σ(Z) (Å)
Fe	0.01901	0.19318	0.25000	0.0014	0.0017	0.0000
C1	0.16155	0.23207	0.30778	0.0063	0.0071	0.0080
C2	0.11489	0.07233	0.35636	0.0074	0.0087	0.0081
C3	0.14679	-0.12259	0.31554	0.0071	0.0075	0.0092
C4	-0.04026	0.33741	0.35683	0.0072	0.0090	0.0083
C5	-0.06720	-0.00523	0.25000	0.0104	0.0139	0.0000
F1	0.19823	0.37705	0.36830	0.0046	0.0050	0.0060
F2	0.10563	0.07201	0.47044	0.0049	0.0057	0.0048
F3	0.23884	-0.17418	0.35343	0.0049	0.0049	0.0060
F4	0.08432	-0.25754	0.35336	0.0050	0.0051	0.0067
O1	-0.07965	0.43299	0.41870	0.0059	0.0069	0.0069
O2	-0.12000	-0.13189	0.25000	0.0076	0.0085	0.0000

TABLE 5.4.

$C_6F_8Fe(CO)_3$: Atomic vibration parameters

The temperature factor (T) is defined by:-

$$T = 2^{-10^{-5}(b_{11}h^2 + b_{22}k^2 + b_{33}\ell^2 + b_{23}k\ell + b_{13}h\ell + b_{12}hk)}$$

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Fe 1	492	2241	958	0	0	- 43
C1	584	2353	1438	- 864	-379	- 128
C2	712	3543	993	480	48	119
C3	679	2418	1805	1220	-103	278
C4	730	3464	1096	-1174	82	162
C5	577	3169	1494	0	0	58
F1	886	3599	2293	-2216	-872	- 98
F2	1076	6318	1087	1259	-190	703
F3	928	3989	2370	1661	-459	1112
F4	1064	3387	2989	3019	567	- 185
O1	1024	5507	1545	-1513	143	570
O2	658	2982	2386	0	0	- 325

TABLE 5.5.

$C_6F_8Fe(CO)_3$: Intramolecular bondlengths and bond-angles (with estimated standard deviations, excluding errors in unit-cell parameters).

Bond	length (Å)	e.s.d. (Å)
Fe - C1	2.060	0.007
Fe - C2	1.993	0.008
Fe - C4	1.803	0.008
Fe - C5	1.799	0.013
C1 - C1'	1.374	0.012
C1 - C2	1.397	0.011
C2 - C3	1.497	0.012
C3 - C3'	1.558	0.013
C1 - F1	1.330	0.009
C2 - F2	1.362	0.010
C3 - F3	1.368	0.009
C3 - F4	1.336	0.009
C4 - O1	1.123	0.011
C5 - O2	1.129	0.015
Intramolecular Contacts:		
Fe - C3	2.890	0.008
F1 - F1'	2.813	0.009
F1 - F2	2.737	0.008
F2 - F3	2.840	0.008
F2 - F4	2.687	0.008
F3 - F4	2.163	0.007
F3 - F3'	2.460	0.009
F3 - F4'	3.275	0.009
F4 - F3'	3.275	0.009

TABLE 5.5. (continued)

Bond	length (Å)	e.s.d. (Å)
F4 - F4'	2.458	0.010
C1 - C4	2.878	0.010
F1 - C4	3.282	0.009
C2 - C2'	2.529	0.012
C2 - C5	2.815	0.012
F2 - C5	3.548	0.009
C4 - C4'	2.540	0.012
C4 - C5	2.714	0.015
O1 - O1'	4.012	0.010
O1 - O2	4.427	0.010

Bond-angles	angle (°)	e.s.d. (°)
C1 - Fe - C1'	39.0	0.3
C1 - Fe - C2	40.3	0.3
C2 - Fe - C2'	78.8	0.3
C4 - Fe - C4'	89.6	0.4
C4 - Fe - C5	97.8	0.4
C2 - C1 - C1'	114.4	0.7
C2 - C1 - F1	122.7	0.8
F1 - C1 - C1'	122.8	0.7
C1 - C2 - C3	116.7	0.7
C1 - C2 - F2	117.0	0.7
F2 - C2 - C3	110.4	0.7
C1 - C2 - Fe	72.4	0.5
F2 - C2 - Fe	125.0	0.5
C3 - C2 - Fe	110.0	0.6

TABLE 5.5. (continued)

Bond-angles	angle (°)	e.s.d. (°)
C2 - C3 - C3'	108.9	0.7
C2 - C3 - F3	112.9	0.7
C2 - C3 - F4	109.8	0.7
F3 - C3 - C3'	109.2	0.6
F3 - C3 - F4	106.2	0.6
F4 - C3 - C3'	109.7	0.7
Fe - C4 - O1	176.1	0.8
Fe - C5 - O2	178.8	1.1

TABLE 5.6.

Intermolecular Contacts to 3.8 Å.

(Only contacts for the asymmetric unit are calculated; the remaining half of the molecule has both atoms and contacts related by reflection across $Z = \frac{1}{4}$).

Atom	Contact	Å
C1	F4 (x, 1+y, z)	3.72
C2	F2 (-x, -y, 1-z)	3.75
C3	F1 (x, 1-y, z)	3.59
C4	O1 (-x, 1-y, 1-z)	3.50
	F2 (-x, -y, 1-z)	3.61
	F3 ($-\frac{1}{2}$+x, -y, z)	3.19
	F4 (x, 1+y, z)	3.27
	F4 (-x, -y, 1-z)	3.54
C5	F2 (-x, -y, 1-z)	3.40
	F2 (-x, -y, $-\frac{1}{2}$+z)	3.40
	F3 ($-\frac{1}{2}$+x, -y, z)	3.15
	F3 ($-\frac{1}{2}$+x, -y, $-\frac{1}{2}$+z)	3.15
O1	O1 (-x, 1-y, 1-z)	3.04
	F1 ($-\frac{1}{2}$+x, 1-y, z)	3.33
	F1 (-x, 1-y, 1-z)	3.27
	F2 (-x, 1-y, 1-z)	3.69
	F2 (-x, -y, 1-z)	3.75
	F3 ($-\frac{1}{2}$+x, -y, z)	3.13
	F4 (x, 1+y, z)	3.18
	F4 (-x, -y, 1-x)	2.97
O2	C1 ($-\frac{1}{2}$+x, -y, z)	3.10
	C1 ($-\frac{1}{2}$+x, -y, $\frac{1}{2}$-z)	3.10
	C3 ($-\frac{1}{2}$+x, -y, z)	3.69

TABLE 5.6. (continued)

Atom	Contact	Å
O2	C3 (-½+x, -y, ½-z)	3.69
	O1 (x, -1+y, z)	3.66
	O1 (x, -1+y, ½-z)	3.66
	F1 (-½+x, -y, z)	3.30
	F1 (-½+x, -y, ½-z)	3.30
	F2 (-x, -y, 1-z)	3.36
	F2 (-x, -y, -½+z)	3.36
	F3 (-½+x, -y, z)	3.10
	F3 (-½+x, -y, ½-z)	3.10
F1	F1 (½-x, y, 1-z)	3.43
	F3 (x, 1+y, z)	3.15
	F4 (x, 1+y, z)	2.96
F2	F2 (-x, -y, 1-z)	3.10
	F3 (½-x, y, 1-z)	3.42
	F4 (-x, -y, 1-z)	3.55
F3	F3 (½-x, y, 1-z)	3.50

TABLE 5.7.

$C_6F_8Fe(CO)_3$: Root Mean Square Amplitudes and Direction Cosines of the Atomic Vibration Ellipsoids

Atom	$\sqrt{(\overline{u^2}_{max.})}$ (Å)	$\sqrt{(\overline{u^2}_{med.})}$ (Å)	$\sqrt{(\overline{u^2}_{min.})}$ (Å)
Fe	0.218 (0.000, 0.000,-1.000)	0.194 (0.111,-0.994, 0.000)	0.177 (0.994, 0.111, 0.000)
C1	0.279 (0.229, 0.290,-0.929)	0.201 (-0.681, 0.730, 0.060)	0.173 (0.696, 0.619, 0.365)
C2	0.252 (0.130, 0.884, 0.448)	0.214 (0.394,-0.461, 0.795)	0.212 (0.910, 0.073,-0.408)
C3	0.309 (-0.026, 0.305, 0.952)	0.214 (0.901, 0.420,-0.109)	0.180 (-0.433, 0.855,-0.286)
C4	0.270 (-0.017,-0.747, 0.665)	0.219 (0.929, 0.234, 0.287)	0.195 (-0.370, 0.622, 0.690)
C5	0.272 (0.000, 0.000,-1.000)	0.231 (0.058, 0.998, 0.000)	0.192 (0.998,-0.058, 0.000)
F1	0.367 (0.270, 0.376,-0.886)	0.244 (0.747,-0.662,-0.053)	0.191 (0.607, 0.648, 0.460)
F2	0.338 (0.208, 0.941, 0.267)	0.265 (0.911,-0.088,-0.403)	0.212 (-0.356, 0.327,-0.876)
F3	0.357 (-0.085, 0.345, 0.935)	0.283 (0.715, 0.675,-0.184)	0.191 (-0.694, 0.653,-0.304)
F4	0.409 (0.137, 0.360, 0.923)	0.262 (0.949,-0.314,-0.018)	0.192 (-0.283,-0.879, 0.384)
O1	0.330 (-0.127,-0.826, 0.550)	0.268 (0.765, 0.271, 0.585)	0.233 (-0.632, 0.495, 0.597)
O2	0.344 (0.000, 0.000,-1.000)	0.230 (0.444,-0.896, 0.000)	0.199 (0.896, 0.444, 0.000)

CHAPTER VI

THE BONDING OF THE BUTADIENE RESIDUE OF CONJUGATED CYCLIC ORGANIC LIGANDS TO TRANSITION METAL IONS.

6.1. The Bonding of the Cyclopentadiene and Cyclopentadienone Ligands to Transition Metals.

Although the only cyclopentadiene complex to be comprehensively studied by single-crystal X-ray diffraction techniques is π-cyclopentadienyl 1-(exo)-phenyl-cyclopentadienecobalt (Chapter III), there have been three independent determinations of complexes containing substituted cyclopentadienone ligands. The salient details of these complexes are summarised below:-

(a) π-cyclopentadienyl tetramethylcyclopentadienonecobalt (Dahl and Smith, 1961).

The cyclopentadienone and π-cyclopentadienyl ligands are almost parallel, the calculated angle between the two planes being 3°. The two rings are in an eclipsed configuration, the perpendicular distances from the cobalt atom to the cyclopentadienone and π-cyclopentadienyl ligands being 1.63 Å and 1.67 Å respectively. The dienone is bent across the line joining C2 and C5 such that the keto-group is tipped out of the plane of the atoms C2, C3, C4, C5 (and away from the cobalt atom) by 9°. The carbon-carbon distances within the cyclopentadienone ring are reported as "essentially equal".

(b) π-cyclopentadienyl tetrakis-(trifluoromethyl)cyclopentadienone-cobalt (Gerloch and Mason, 1964; Gerloch, 1964).

The trifluoromethyl analogue of (a) is forced into the staggered conformation by inter-annular fluorine-hydrogen contacts. The cyclopentadienone ligand is bent across C2-C5 by 21.3°, such that the keto-group is further from the metal than the other carbon atoms of the dienone ligand. The bondlengths around the cyclopentadienone (using the standard numbering, with the keto-group identified as C1) are:-

C1-C2 = 1.49 Å, C1-C5 = 1.50 Å;
C2-C3 = 1.40 Å, C4-C5 = 1.49 Å;
C3-C4 = 1.43 Å.

The cyclopentadienone and π-cyclopentadienyl ligands are, respectively, 1.62 Å and 1.68 Å distant from the metal. The internal angle at the keto-group (i.e. C2-C1-C5) is 100.1°.

(c) tetrakis(trifluoromethyl)cyclopentadienone iron tricarbonyl (Bailey, Gerloch and Mason, 1964; Bailey, 1964).

Bondlengths around the cyclopentadienone ligand are:-

C1-C2 = 1.46 Å, C1-C5 = 1.50 Å;
C2-C3 = 1.37 Å, C4-C5 = 1.42 Å;
C3-C4 = 1.40 Å.

The internal angle at the keto-group is 101.5°. The angle of bend across C2-C5 is 20.1°. The bonds to the dienone are staggered with respect to the three carbonyl groups, with one carbonyl group passing immediately below the keto-group. The atoms C2, C3, C4, C5 form a plane distant 1.67 Å from the iron atom.

In each of the above cases there is some contribution from localized bonding in the attachment of the cyclopentadienone ligand to the metal (as is evidenced by the non-planarity of the dienone). In strict valence-bond terminology the ligand is to be regarded as either:-

(i) bonded by two π-bonds, with the metal in a +m valence state, or

(ii) bonded by one π-bond and two σ-bonds, the metal now being in a formal +(m+2) valence state.

The variation in the angle of tilt in the cyclopenta-diene (or -dienone) ligand between the limits 9° (in π-$C_5H_5.Co.(CH_3)_4C_5O$) and 36.5° (in π-$C_5H_5.Co.C_5H_5.C_6H_5$) quickly exposes the limitations of the valence-bond method in the present context. Thus, one can talk only of the 'degree of localization' in the bonding. It follows that there should be some direct relationship between the nature of the molecule considered and the degree of localization actually present. π-cyclopentadienyl 1-phenylcyclopentadienone cobalt has all the features of a compound in which the valence-bond description of one π- and two σ- bonds is almost true, since:-

(a) the diene ligand shows the greatest degree of bend (and the carbon atoms C2 and C5 more nearly approach the 'ideal' tetrahedral environment);

(b) the bondlengths around the cyclopentadiene ring show only one double and four single bonds;

(c) the 'squeeze-angle' at C1 is 93.9° showing that the carbon atoms C2 and C5 are strongly involved in localized bonding;

(d) the n.m.r. spectrum is completely consistent with the formulation of the compound as a σ- and π- bonded complex.

The dienones exhibit a definite graduation in the relative amount of localized bonding present. The variable parameters considered in this context in a qualitative manner are:-

(i) the localization energy of the parent ligand, i.e. the energy required to localize charge at C2 and C5 in the ligand considered;

(ii) stereochemical and charge requirements of the metal;

(iii) any effects due to the ligand opposite the cyclopentadienone preferentially stabilizing, or de-stabilizing, the localization of charge on the dienone ligand.

Fortunately, having available structural data for both $\pi\text{-}C_5H_5Co(CH_3)_4C_5O$ and $\pi\text{-}C_5H_5Co(CF_3)_4C_5O$ leads to the parameter (i) being immediately answered. Thus, whereas the trifluoromethyl-substituted ligand (in which four CF_3-groups are removing a considerable amount of charge from the delocalized system) forms a complex in which the dienone distorts by 21.3°, the methyl-substituted ligand (in which the inductive effect of the four CH_3-groups will be to increase the charge density around the delocalized system) forms a complex in which the distortion is only 9°. Consequently, one immediately observes that:-

the lower the dolocalization energy in the conjugated olefinic system, the easier is the accumulation of charge at the potential σ-bonding centres and the greater is the contribution of the σ- and -π- bonded form to the final molecular structure.

A comparison of the structures of $(CF_3)_4C_5O.Co.\pi\text{-}C_5H_5$ and $(CF_3)_4C_5O.Fe(CO)_3$ shows that the substitution of a $\pi\text{-}C_5H_5Co.$ group by an $Fe(CO)_3$ group results in a decrease in the distortion of the ligand from 21.3° to 20.1°. Since this difference is on the borderline of statistical significance (~ 1.3σ) it is difficult to estimate the effects of the metal and the ligand opposite to the dienone.

If the decrease <u>is</u> considered significant then it may be argued that:-

(a) the two -π- bonded representation for the cyclopentadienone ligand leads to a 5-coordinate system in each of the cases concerned. Since zero-valent 5-coordinate iron is well-established and Fe(0) vs. Fe(+2) is not normally as unfavourable as Co(+1) vs. Co(+3), it would be expected that the $\pi\text{-}C_5H_5Co.$ compound would contain a greater contribution from localized bonding than would the $Fe(CO)_3$ derivative;

(b) the carbonyl groups are probably better as regards stabilizing a low valence state (as judged by frequency of occurrence of low valence-state carbonyls *vis à vis* low valence-state π-cyclopentadienyls). Consequently, once again, the cobalt complex would be expected to contain a greater contribution from localized bonding than would the iron compound.

It must be emphasized, however, that, according to the available data, the identity of the metal and the nature of other ligands attached to this metal have only a second-order effect in dictating the rôle of localized bonding to the diene ligand considered.

Although the cyclopentadienone complexes are fairly well understood, the cyclopentadiene complexes create a quite new problem. The 1-phenylcyclopentadiene ligand is bent through 36.5° on bonding to a transition metal, but the simple unsubstituted compound is probably (assuming the $C-H_{\alpha}$ stretch is correctly assigned and explained) much closer to a planar conformation. The only simple way of explaining these observations is to assume that the phenyl-group in the $C_5H_5.C_6H_5$ ligand has a large inductive effect and that charge is being removed from C1 in such a way as to reduce the delocalization around C2, C3, C4, C5 by a purely inductive effect. A planar C_5H_6 ligand in π-$C_5H_5.Co.C_5H_6$ could then be explained on the basis of hyperconjugation of the methylene group, which would effectively increase the aromaticity of the cyclopentadiene ligand.

6.2. The Bonding of Conjugated Six-Membered Rings to Transition Metals.

The controversy surrounding the bonding of the benzene ligand to the metal in bisbenzenechromium has been resolved (Cotton, Dollase and Wood, 1963; Cotton, 1964) in favour of a completely delocalized benzene system. A similar conclusion has been reached with the structures of benzenechromium tricarbonyl (Corradini and Allegra, 1959) and hexamethylbenzenechromium tricarbonyl (Dahl, 1964).

The structure of π-cyclopentadienyl hexakis(trifluoromethyl) benzene rhodium is thus the only known example (apart, possibly from its cobalt analogue; Cox and Wilkinson, 1964) in which the benzene ring is not symmetrically bonded to the ligand. Although quantitative results are extremely difficult to obtain, the resonance energy within the benzene ring must be very considerably reduced in the trifluoromethyl substituted nucleus. It is entertaining to note that all attempts to prepare transition-metal complexes directly from hexafluorobenzene have proved fruitless and it seems highly probable that these complexes in which the aromatic ring has a low resonance energy may have to be 'built-up' on the metal as is π-$C_5H_5.Rh(CF_3)_6C_6$ (Dickson and Wilkinson, 1963; idem 1964).

The distortion from planarity of 47.3° in the cyclohexadiene ring of octafluoro-cyclohexa-1,3-diene iron tricarbonyl (Chapter V) is almost identical to the value of 47.9° calculated for the hexakis(trifluoromethyl)benzene complex of rhodium. Since fluorine is the most electronegative substituent possible to substitute into the butadiene system it seems probable that each of these complexes is, in fact, in the completely localized form. However, the similarity of bondlengths around the butadiene portion of the ligand indicates that the valence-bond method has its limitations even at one extreme of the degree-of-localization scale (see Section 6.4).

6.3. The Bonding to Transition Metal Ions of Conjugated Dienes contained within Seven- and Eight- Membered Rings.

The compound 2,4,6-triphenylcycloheptatrienone iron tricarbonyl (Smith and Dahl, 1962), shows the same general features as do the other butadiene-containing compounds mentioned previously. The angle of distortion, now defined by the deviation of the plane C4-C5-C6-C7 from that formed by C7-C1-C2-C3-C4 is now 41° (i.e. complete localization is not present, since the angle of distortion will tend to increase with increasing ring size). Although the structure of the unsubstituted compound cycloheptatrienone iron tricarbonyl has been studied by Dodge and Schomaker (see Smith and Dahl, 1962) and the same sense of distortion is known to occur, the exact values are not available and, unfortunately, the effect of the three phenyl groups on the ease of localization at C4 and C7 cannot be ascertained. This would certainly be valuable since, at present the effect of the phenyl-group in π-cyclopentadienyl 1-phenylcyclopentadienecobalt is not fully understood.

Cycloheptatriene molybdenum tricarbonyl (Dunitz and Pauling, 1960) contains a non-planar ligand, but the triene system itself is planar with an alternating system of double and single bonds. The system cannot be regarded as bonding via 2π- and 2σ- bonds and it seems that, in this complex at least, the major requirement is the octahedral coordination of the molybdenum atom, which is easily brought about by three bonds to carbonyl groups and three bonds to localized olefinic sites.

Cyclo-octatetraene forms complexes with one and two $Fe(CO)_3$ groups respectively. $C_8H_8Fe(CO)_3$ (Dickens and Lipscomb, 1961 b; idem 1962) exists in the dihedral form common to other complexes in which there is a large degree of localization. The cyclo-octatetraene ring in $(OC)_3FeC_8H_8Fe(CO)_3$ (Dickens and Lipscomb 1961 a; idem 1962) exists in a novel chair form in which each of the $Fe(CO)_3$ groups can be regarded as forming one π- and two σ- bonds with the ligand. In each complex the angle of bend is approximately 41°.

6.4. A Molecular Orbital Approach to Localized Bonding.

Once it had been realised that with ligands of a given ring size the energy of localization was the most important feature of conjugated olefinic systems it seemed necessary that some molecular orbital calculations should be performed in order to put the observations on a semi-quantitative basis. These were originally performed for benzene using a simple Hückel approach. Hexamethylbenzene- and benzene- transition metal complexes are known to have planar six-membered rings, whereas the hexakis(trifluoromethyl)benzene ring is known to be decidedly non-planar in $\pi\text{-}C_5H_5Rh(CF_3)_6C_6$.

Using the normal Hückel approximations

(i) all overlap integrals S_{nm} = zero;

(ii) all orbitals are normalized S_{mm} = unity;

(iii) all integrals H_{nn} are the same; $H_{11} = \alpha$ (the coulomb integral);

(iv) all integrals H_{nm} involving non-adjacent atoms are put = zero; involving adjacent atoms $H_{n,n+1} = \beta$ (the resonance integral).

For benzene the secular determinant:-

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} & H_{14}-ES_{14} & H_{15}-ES_{15} & H_{16}-ES_{16} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} & H_{24}-ES_{24} & H_{25}-ES_{25} & H_{26}-ES_{26} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} & H_{34}-ES_{34} & H_{35}-ES_{35} & H_{36}-ES_{36} \\ H_{41}-ES_{41} & H_{42}-ES_{42} & H_{43}-ES_{43} & H_{44}-ES_{44} & H_{45}-ES_{45} & H_{46}-ES_{46} \\ H_{51}-ES_{51} & H_{52}-ES_{52} & H_{53}-ES_{53} & H_{54}-ES_{54} & H_{55}-ES_{55} & H_{56}-ES_{56} \\ H_{61}-ES_{61} & H_{62}-ES_{62} & H_{63}-ES_{63} & H_{64}-ES_{64} & H_{65}-ES_{65} & H_{66}-ES_{66} \end{vmatrix} = 0$$

reduces to:-

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0$$

Allowance for substituents on the benzene ring can be made by substituting $(\alpha+m\beta)$ for α in the above equations. The most probable parameter for a carbon atom with a methyl group substituted on it is $(\alpha_c -0.15\beta)$; although the exact form for a trifluoromethyl group is unknown, the electronegativity is somewhere between that of fluorine and chlorine and a sensible value for the Coulomb integral is $(\alpha_c +0.20\beta)$.

The values of the energy levels of the molecules have been calculated for all values $\alpha = \alpha_c \pm 0.25\beta$ by steps of 0.05β:-

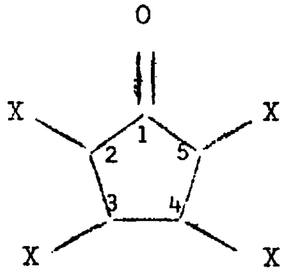
Parameters	Energy Level Coefficients					
	$E_i = \alpha + m_i\beta$					
	m_3	m_2	m_1	m_{-1}	m_{-2}	m_{-3}
$\alpha + 0.25\beta$	2.25	1.25	1.25	-0.75	-0.75	-1.75
$\alpha + 0.20\beta$	2.20	1.20	1.20	-0.80	-0.80	-1.80
$\alpha + 0.15\beta$	2.15	1.15	1.15	-0.85	-0.85	-1.85
$\alpha + 0.10\beta$	2.10	1.10	1.10	-0.90	-0.90	-1.90
$\alpha + 0.05\beta$	2.05	1.05	1.05	-0.95	-0.95	-1.95
α	2.00	1.00	1.00	-1.00	-1.00	-2.00
$\alpha - 0.05\beta$	1.95	0.95	0.95	-1.05	-1.05	-2.05
$\alpha - 0.10\beta$	1.90	0.90	0.90	-1.10	-1.10	-2.10
$\alpha - 0.15\beta$	1.85	0.85	0.85	-1.15	-1.15	-2.15
$\alpha - 0.20\beta$	1.80	0.80	0.80	-1.20	-1.20	-2.20
$\alpha - 0.25\beta$	1.75	0.75	0.75	-1.25	-1.25	-2.25

It can easily be seen for benzene complexes that whilst the lowest unfilled orbital m^{-}_{1} is at a value $E^{-}_{1} = \alpha - 1.15\beta$ for hexamethyl benzene, this value is lowered to $\alpha-\beta$ for an unsubstituted benzene nucleus and is decreased still more (to $\alpha - 0.80\beta$) for hexakis(trifluoromethyl)benzene. Thus the more electronegative the substituents around the benzene ring, the less antibonding in character is the lowest unfilled level.

Consequently, back-donation (from the metal to this antibonding orbital) will be enhanced. Since, in molecular-orbital theory the valence bond approach of π-bonding vs. σ- and π- bonding is replaced by π-forward bonding vs. π-back-donation, the greater the degree of back-donation then the greater the degree of localization of charge. At the present time, however, it must be admitted that although this picture has some advantage (i.e. it is basically more realistic), it seems difficult to actually correlate the degree of bending in the ligand with the degree of localization of charge due to back-donation.

The variation of the molecular orbital energy levels with substituents of varying electronegativity is demonstrated much more successfully by the cyclopentadienone complexes.

The parameters used are:-



$$\alpha_o = \alpha_c + 0.8\beta$$

$$\alpha(C_1) = \alpha_c + 0.1\beta$$

$$\beta_{c=o} = 1.1\beta_{c=c}$$

Again, the molecular energy levels have been calculated by integral steps of 0.05β between the limits $\alpha(C2, C3, C4, C5) = \alpha_c \pm 0.25\beta$.

Parameters	Energy Levels $(E_i = \alpha + m_i\beta)$					
	m_3	m_2	m_1	$m_{\bar{1}}$	$m_{\bar{2}}$	$m_{\bar{3}}$
$\alpha + 0.25\beta$	2.41	1.45	0.87	0.21	-1.37	-1.66
$\alpha + 0.20\beta$	2.38	1.42	0.82	0.19	-1.42	-1.69
$\alpha + 0.15\beta$	2.35	1.40	0.77	0.16	-1.47	-1.71
$\alpha + 0.10\beta$	2.32	1.37	0.72	0.14	-1.52	-1.73
$\alpha + 0.05\beta$	2.30	1.35	0.67	0.11	-1.57	-1.75
α	2.27	1.32	0.62	0.09	-1.62	-1.78
$\alpha - 0.05\beta$	2.25	1.29	0.57	0.06	-1.67	-1.80
$\alpha - 0.10\beta$	2.22	1.26	0.52	0.04	-1.72	-1.83
$\alpha - 0.15\beta$	2.20	1.24	0.47	0.02	-1.77	-1.85
$\alpha - 0.20\beta$	2.18	1.21	0.42	0.00	-1.82	-1.88
$\alpha - 0.25\beta$	2.16	1.19	0.37	-0.02	-1.87	-1.90

The effect of substitution around the ligand by the trifluoromethyl groups is to depress the energy of the highest filled molecular orbital and hence to decrease the π-electron donor characteristics of the ligand. Simultaneously the 'electron affinity' of the ligand is increased by a decrease in energy of the lowest unfilled molecular orbital (m_{-1}). In fact, the energy of this lowest unfilled molecular orbital is such that it is, in fact, a bonding orbital (i.e. m_{-1} is positive) so that electron donation to this level will be particularly favoured.

Using the information from the previous tables, we see the greater amount of back-donation from the metal which occurs for the more electronegative ligands. There can obviously be the gradation from complexes in which the bonding is (mainly) forward from ligand to metal through to those in which there are approximately equal amounts of forward bonding and back-donation.to those in which the larger part of the bonding is due to back-donation. Most of the complexes studied may (as a last approximation) be treated in a manner analogous to butadiene. In forward bonding the molecule behaves as if in its ground state; in back-donation, the first excited state is involved. Since the π-bond orders for butadiene are 0.89, 0.45, 0.89 in the ground state and 0.45, 0.67, 0.45 in the first excited state it follows that suitable combinations of forward- and back- bonding can lead to the bondlengths observed in the octafluorocyclohexadiene complex (1.40, 1.37, 1.40 Å; Chapter V). Thus, although from a valence-bond picture this molecule is regarded as having a C_6F_8 ligand bonding by two σ- and one π- bonds, the molecular orbital description gives a more realistic description of the bond-order within the ligand.

6.5. Summary and Conclusions

The crystal structures of three conjugated olefin complexes of transition metals have been studied and accurate molecular dimensions and stereochemistry obtained. A careful study of systematic variations in the geometry of these complexes and a comparison with other structures has led to a set of empirical rules which describe (and can be used to predict) the conformation of a series of organic ligands when bonded to a (given) metal. The valence-bond method has been used throughout the text and a comparison with molecular orbital theory is finally shown to lead to the same results (with some advantages, such as an explanation of bondlengths within a ligand). It must be emphasized that there are far more variables that eventually must be considered. Although the distortion of $(CF_3)_4C_5O$ has been found to vary little on bonding to iron and cobalt, no study has been made of the effect of metals from different transition series on the same ligand. Since cyclic organic ligands are distorted in such a way as to maximize their overlap integrals with the metal, it follows that metals from different transition series will preferentially stabilize different organic ligands. From a study of the covalent radii it is obvious that the preferred separation of two ligands (e.g. two σ-bonding carbon atoms) bonded to a $3d^24s4p^3$ hybridized

Co(+3) ion will be smaller than will the separation with a $4d^2 5s 5p^3$ hybridized Rh(+3) ion. It is therefore quite possible that the maximum overlap for a Co(+3) ion occurs with localized bonds to the 2 and 5 positions of a cyclopentadiene ligand (C2-C5 = 2.25 Å in π-$C_5H_5CoC_5H_5C_6H_5$) whereas, for a Rh(+3) ion, localized bonding to the 1 and 4 positions of a cyclohexadiene (or benzene) ligand will be more favourable (C1-C4 = 2.56 Å in π-$C_5H_5RhC_6(CF_3)_6$). In this context, it is interesting to note that the reaction of hexafluorobut-2-yne with the cobalt and rhodium π-cyclopentadienyl carbonyl leads to different proportions of the two observed products : with π-$C_5H_5Co(CO)_2$ the cyclopentadienone complex, π-$C_5H_5Co(CF_3)_4C_5O$, is preferentially formed with only a trace of π-$C_5H_5CoC_6(CF_3)_6$; with π-$C_5H_5Rh(CO)_2$, however, almost equal quantities of the dienone and benzene complexes are produced.

It is likely, therefore, that the degree of localization in the bonding of a ligand will differ with elements from different transition series. Thus the bonding of the cyclopentadiene ligand in π-$C_5H_5CoC_5H_5C_6H_5$ and the isomorphous (Angelici and Fischer, 1963) π-$C_5H_5RhC_5H_5C_6H_5$ will be substantially different. Unfortunately, to obtain confirmation of these conclusions, the complete crystal structures of a large number of related compounds must be studied. Since consolidation of data is a time-consuming occupation, it is unlikely that these structures will be investigated until automatic diffractometers become standard equipment in the crystallographic laboratory.

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