SOME MOLECULAR STRUCTURES BY ELECTRON AND X-RAY DIFFRACTION

Thesis by

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Abstract

Two polycyclohydrocarbons, norbornane and the compound $C_{12}H_{14}$ of De Vries and Winstein, were investigated by electron diffraction. For both molecules the C-C bond was found to be lengthened from the normal value of 1.54 A. Bond strain calculations were made for both molecules.

An electron diffraction investigation of ferrocene confirmed the proposed sandwich structure. The following distances for a model with $D5_d$ symmetry were derived by the correlation method: Fe-C, 2.064 A; C-C, 1.440 A. Both models in which the rings were allowed to rotate with a small potential barrier and models in which the inter-ring C...C distances were assigned a moderately large vibrational temperature factor constant, with no rotation, were found to be consistent with the visual data.

The crystal structure of cyclopentadienyl manganese tricarbonyl was studied by X-ray diffraction. The crystal was treated as a heavy atom problem and three-dimensional methods were used. Anisotropic temperature factors were calculated from a difference Fourier synthesis. The positional parameters were refined by least squares. The $Mn(CO)_3$ part of the molecule has nearly trigonal symmetry and the ring was found to be nearly planar. The packing of the molecules approximates a cubic closest packed array of spheres.

Cyclopentadienyl nickel nitrosyl was investigated by electron diffraction. The method of least squares was used in order to refine the parameters and to estimate the limits of error. Both models with a linear Ni-N-O bond and models with a bent Ni-N-O bond were found to be acceptable. Bond distances in metal carbonyls and related compounds are discussed.

TABLE OF CONTENTS

I*. Electron Diffraction Investigations of Two Polycyclohydrocarbons - Norbornane and the Compound $C_{12}H_{14}$ of De Vries and Winstein

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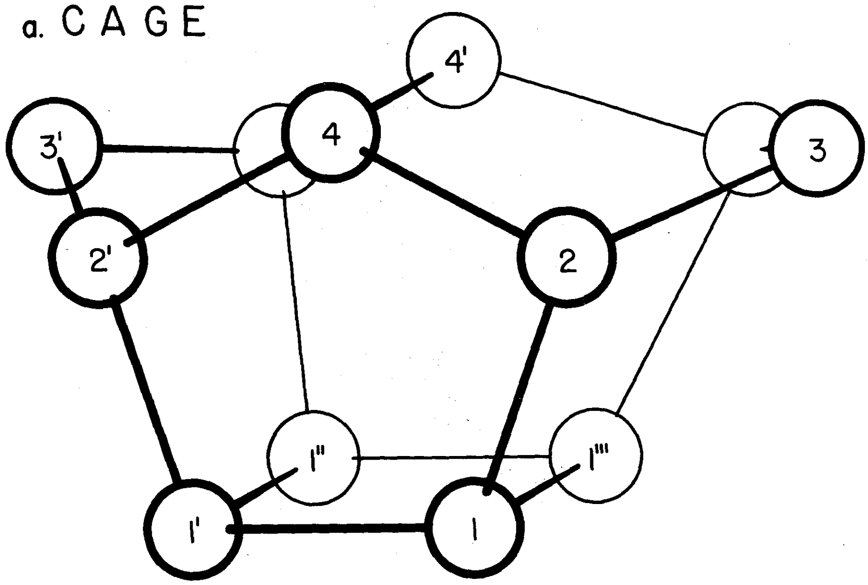
* The work described in this section was done in collaboration with Mr. C. Wong.

The compound $C_{12}H_{14}$ was synthesized by De Vries and Winstein at UCLA (1). They proposed a structural formula (fig. 1a) based solely on the method of preparation. Because of its cage-like appearance and for lack of a more suitable name, we have called it the "cage". Initial X-ray crystallographic work on this compound failed to yield a structure because of rotation of the molecule in the crystal (2), and a low temperature study has as yet not been seriously attempted. Therefore, in spite of the formidable number of parameters, it was felt that a careful electron diffraction study would provide a useful test of De Vries and Winstein's model and would provide information on bonding in polycyclic systems.

The preliminary measurements indicated an unexpected lengthening of the average C-C single bond (see later text) from its normal value of 1.54 A. This result drew our attention to the effect of cross-ring repulsion which has been considered to be the main cause of lengthening of the C-C single bond in cyclobutane (3). At this time Professor Winstein agreed that an investigation of norbornane (bicyclo-2,2,1-heptane, (fig. 1b)), a compound of known structural formula which has similar structural features with the proposed cage model, would be useful, and he supplied the necessary impetus by giving us a sample.

In the study of the related compound nortricyclene (4), the possible lengthening of the C-C bond in the five-membered rings was masked by the interactions between the C-C bonds in the cyclopropane and cyclopentane rings.

a. CAGE



b. NORBORNANE

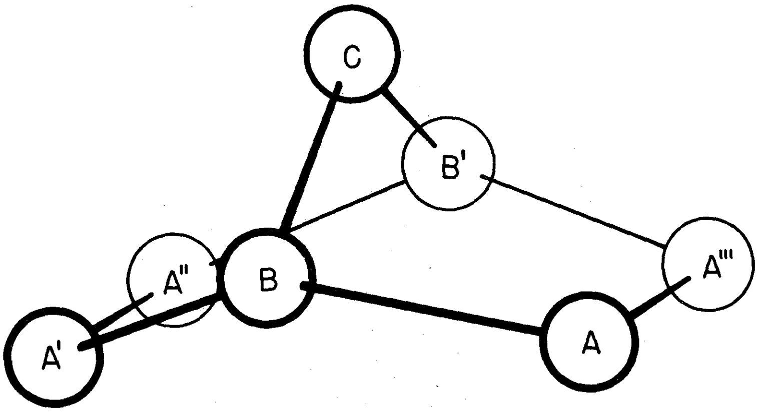


Figure 1

The experimental work is an attempt to answer the following questions: Does the cage really have structural features similar to norbornane? What can be said in detail about the structures of the cage and norbornane? Is the C-C bond length in norbornane also stretched?

Diffraction photographs (Kodak 50 plates) were taken of the cage and norbornane* ($\lambda \approx$ 0.06 A, $\ell \approx$ 10 cm). The diffraction patterns were interpreted visually in the usual manner (5).

The visual curves (fig. 2)** for the cage and norbornane exhibit many similar features, although the pattern of the cage shows the more pronounced high frequency terms. The radial distribution curves (RDI)*** for both molecules have two similar main peaks, a sharp

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* Sample-bulb temperatures:
Cage $\approx$ 115°C
Norbornane $\approx$ -10°C

** Curves A (Cage), V.S.
Curves B (Norbornane), C.W.

All three investigators independently examined the plates and they agreed on the main features of both compounds. However, in the case of the cage, A.B. and C.W. overlooked several fine features of the pattern because of inexperience and in addition the curve of A.B. suffers from several exaggerations. Curve V.S. extends to larger q values. For norbornane curve A.B. suffers the same shortcomings as above, while C.W. and V.S. are in excellent agreement except for two features. The dashed lines in fig. 2 show the interpretation by V.S. for these two features.

*** Distances for the cage beyond 4 A are not shown on the RDI.

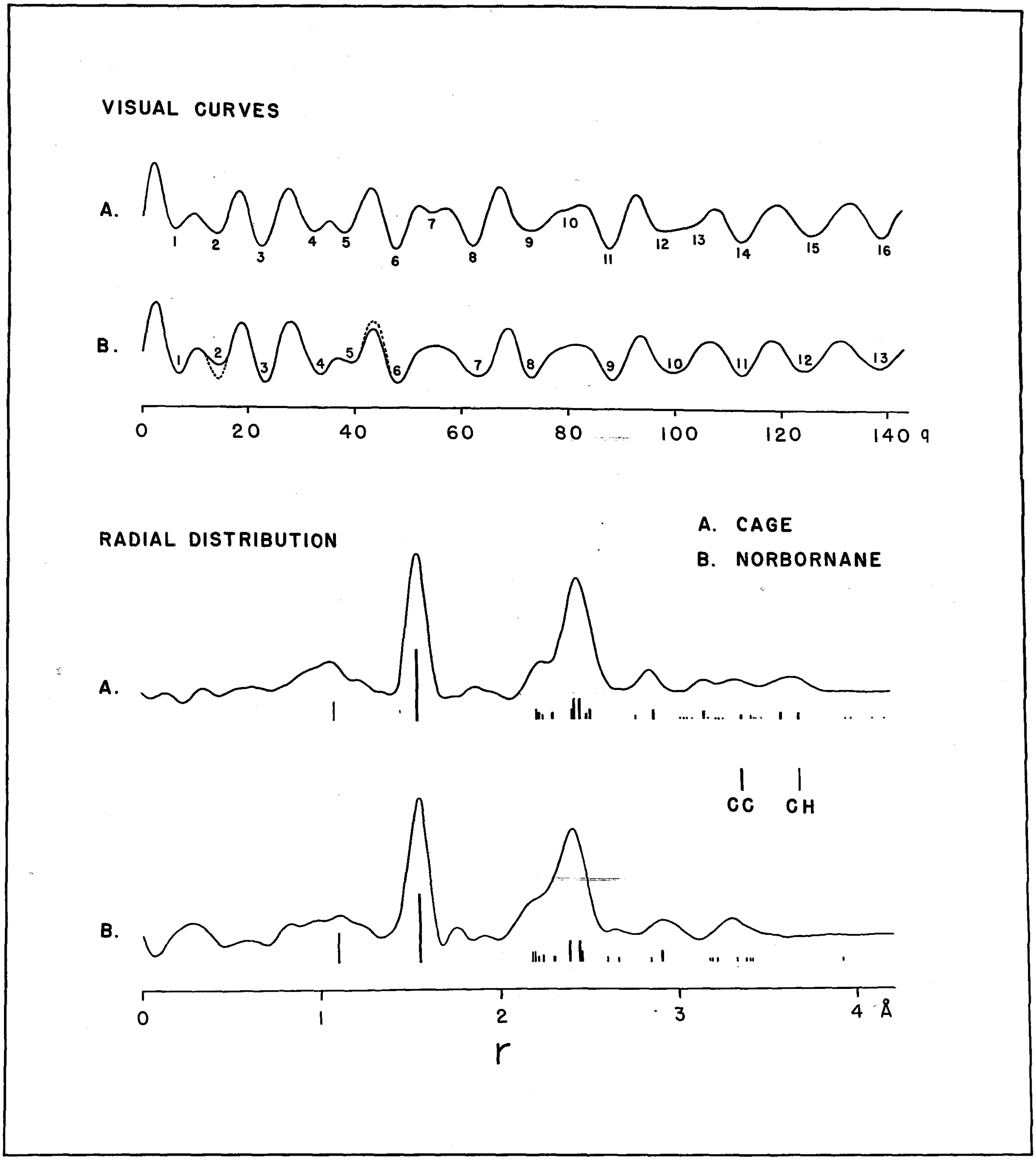
VISUAL CURVES
A.
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
B.
1
2
3
4
5
6
7
8
9
10
11
12
13
0
20
40
60
80
100
120
140 q
RADIAL DISTRIBUTION
A. CAGE
B. NORBORNANE
A.
CC
CH
B.
0
1
2
3
4 Å
r

Figure 2

peak around 1.56 A and a broader peak around 2.45 A, indicative of the presence of puckered five-membered rings. The visual curves and RDI's thus confirm the structural similarity between these two compounds and indicate a lengthening of the average C-C single bond in both.

In order to make any detailed conclusion concerning the proposed cage-like model, and to obtain structural parameters of interest for both molecules, the correlation method was employed to refine the parameters deduced from the structural formulae (fig. 1) and the RDI's.

On the assumption of C_{2v} symmetry, the carbon skeleton of the cage has nine parameters, and the norbornane skeleton five parameters. As a first approximation, all bonded C-C distances were assumed equal, leaving for the cage a four-parameter problem (one scale factor and three shape parameters), and for norbornane a three-parameter problem (one scale factor and two shape parameters). The three shape parameters for the cage are taken as $\measuredangle$ 2-4-2', $\measuredangle$ 2-3-2''' (fig. 1a), and the dihedral angle γ between plane 2-3-2''' and the plane bisector of the dihedral angle formed by planes 4-4'-2'''-2 and 1-1'''-2-2''', which is taken as positive if atom 3 lies on the same side of the plane bisector as atom 4. The two shape parameters for norbornane are $\measuredangle$ B-C-B' and $\measuredangle$ A-B-A' (fig. 1b).

In the case of the cage, the initial assumption of $\gamma = 0$ seems reasonable in view of the approximate symmetry of the molecule about the 2-3-2''' plane. The remaining two-parameter problem was then extensively investigated.[*] Representative theoretical curves in the range $103^\circ < \sphericalangle 242' < 109^\circ$ and $89^\circ < \sphericalangle 232''' < 99^\circ$ are shown by curves 1-8 in fig. 3. (The parameters used in calculating these models are tabulated in Table 1.)

For $\gamma = 0$ the range of acceptability may be interpreted as follows. Features below $q = 40$ are essentially invariant over the range of parameters illustrated. The observation that minimum 8 is deeper than the average of minima 6 and 9[**] is not represented satisfactorily by curves 6, 7, and 12.[***] Curve 5 is on the borderline. The acceptability of this feature is improved in the direction of curves 1, 2 and 8. The shape of minimum 9 was observed to be round and broad and is not represented satisfactorily by curves 7, 8 and 12.[***] Curve 1[****] was judged to be unacceptable since maximum 12 lies inside the broad minimum

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[*] In both compounds the C-H bond length was taken to be 1.09 A. Hydrogen atoms bonded to bridge-head carbon atoms were assumed to be equidistant from the three carbon atoms bonded to the bridge-head atoms, and hydrogen atoms bonded to secondary carbon atoms were symmetrically placed with $\sphericalangle$ H-C-H equal to 109° 28'. (These are very rough approximations.)

[**] A three-fold comparison in which the features compared do not have the same shape is subject to systematic error. However, in this case, careful direct comparisons with the corresponding features for norbornane (fig. 2) were made, so that we are rather confident of our assessment of minima 6, 8 and 9.

[***] Not shown.

[****] Also curves 11 and 12 which are not illustrated.

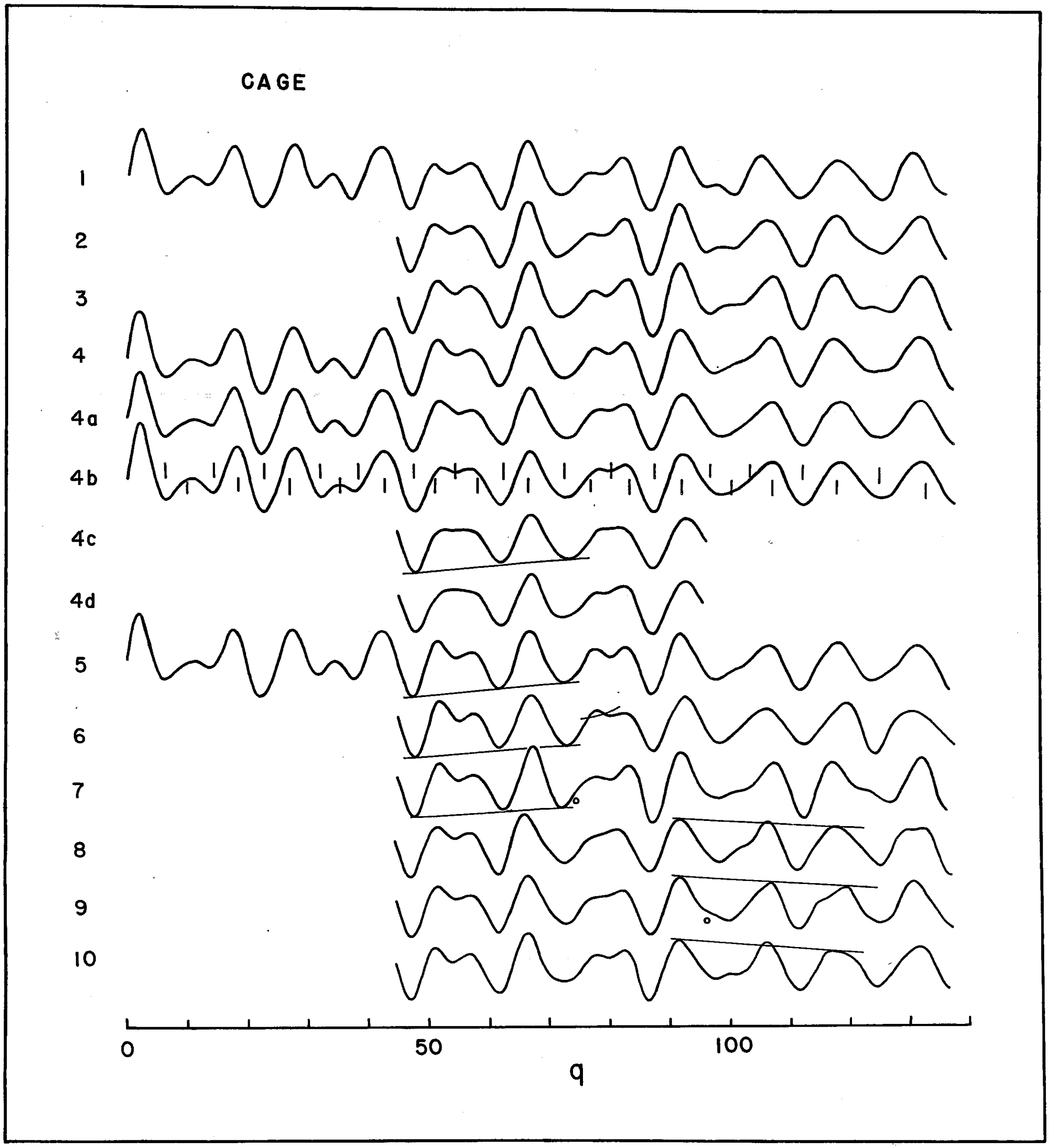

Figure 3

Table 1

Cage Parameters of Fig. 3

Model	$\measuredangle 232'''$	$\measuredangle 242'$	γ	$a_{C.C}^{1}$	$a_{C..C}^{2}$	a_{C-H}	$a_{C.H}^{1}$	$a_{C..H}^{2}$
				($10^4 A^2$)	($10^4 A^2$)	($10^4 A^2$)	($10^4 A^2$)	($10^4 A^2$)
1	89.8	106.5	0	0	0	∞	∞	∞
2	91.2	"	"	"	"	"	"	"
3	93.4	"	"	"	"	"	"	"
4	95.5	"	"	"	"	"	"	"
4a	"	"	"	4.5	7.0	"	"	"
4b	"	"	"	4.5	7.0	23	35	35^3
4c	"	"	"	10.1	10.1	23	35	35^3
4d	"	"	"	4.5	7.0	16	25	25^3
5	96.6	"	"	0	0	∞	∞	∞
6	98.3	"	"	"	"	"	"	"
7	95.5	103.5	"	"	"	"	"	"
8	95.5	109.6	"	"	"	"	"	"
9	95.5	106.5	-5°	"	"	"	"	"
10	95.5	106.5	$+5^\circ$	"	"	"	"	"
11^4	90.4	109.6	0	"	"	"	"	"
12^4	90.4	103.5	0	"	"	"	"	"

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[1] Bonded to the same atom.

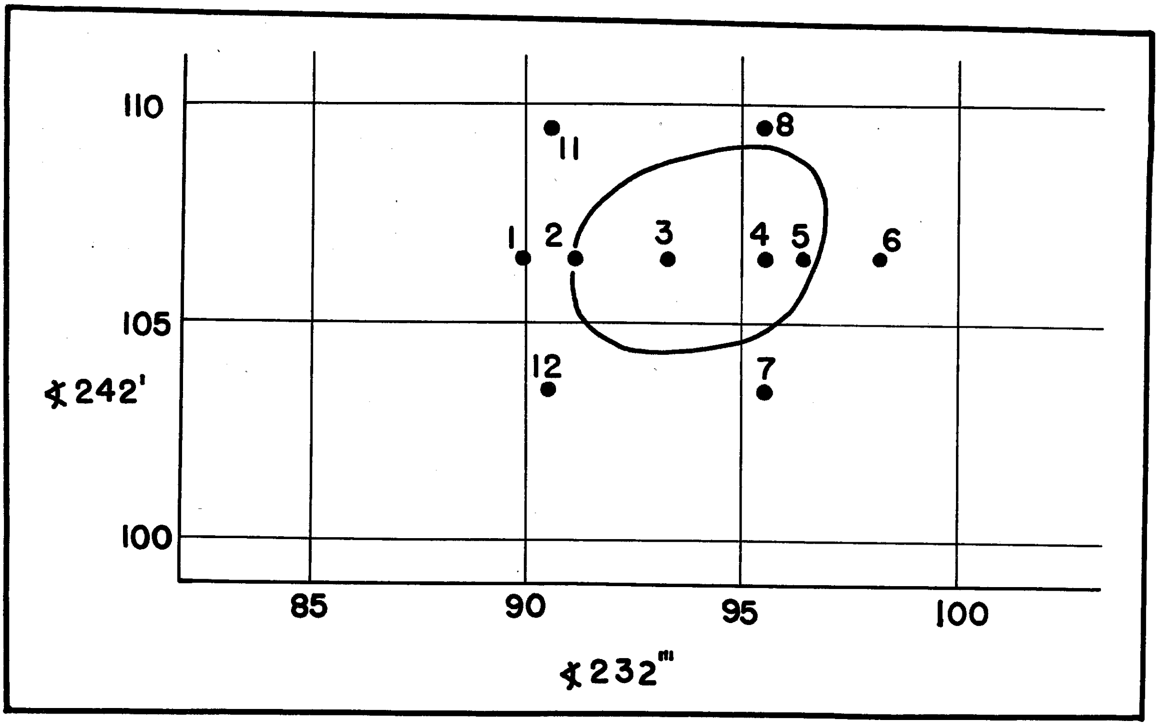
[2] Not bonded to the same atom.

[3] For individual values see Table 2.

[4] Not illustrated in fig. 3.

between maxima 11 and 13 and curve 2 is on the borderline. Increasing $\measuredangle 232'''$ makes this feature acceptable. On curves 8 and 11 maximum 13 is above the average of maxima 11 and 14 which does not represent the visual observations satisfactorily. Minimum 15 is too sharp and deep on curves 1 and 6 and this feature cannot be improved, we believe, by changing the temperature factors. The general appearance of minimum 15 on curves 7 and 8 is not satisfying. The range of acceptability, assuming $\gamma = 0$, is illustrated in fig. 4a. For models inside the range of acceptability, excellent agreement with the visual curve can be obtained by adjusting temperature factors and including hydrogen tests, as shown by curve 4b.

Curves 4, 9 and 10 illustrate the effect of variation of γ. The three-fold comparison among minima 6, 8 and 9 is improved by increasing γ (curve 10) while decreasing γ (curve 9) has no significant effect. Maximum 12 is shifted to the inside of the broad minimum between maxima 11 and 13 by decreasing γ. The three-fold comparison among maxima 11, 13 and 14 becomes unsatisfactory by varying γ in either direction. Curve 9 is unacceptable while curve 10 is barely acceptable. Therefore for the values of $\measuredangle 232'''$ and $\measuredangle 242'$ for model 4, the indication is that $\gamma = +1^\circ \pm 4^\circ$. It is indicated that curve 5 may be made completely acceptable by slightly increasing γ since the three-fold comparison among minima 6, 8 and 9 may be made acceptable without destroying the acceptability of the comparison among maxima 11, 13 and 14.



a. Cage

b. Norbornane

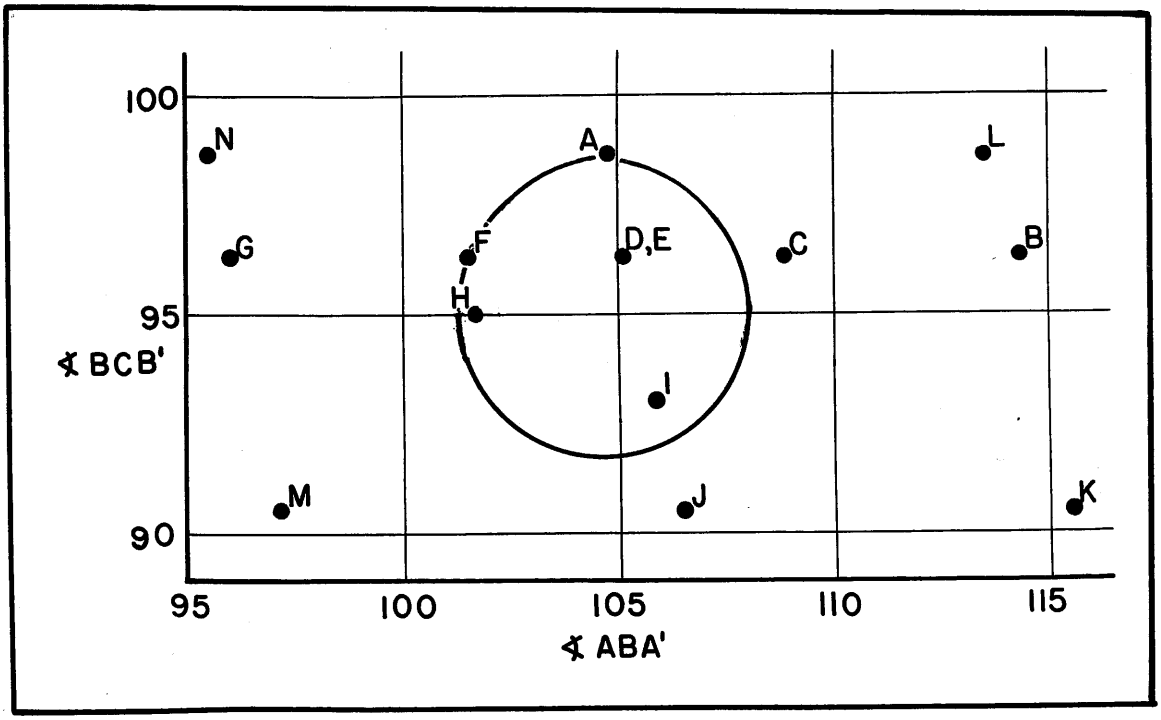


Figure 4

Table 2

Interatomic Distances for Cage model 4b

	Terms	Multiplicity	Distances A	a_{ij} 10^4A^2
I	C-C	17	1.56	0
II	C.C			
	1-4	4	2.42	4.5
	2-4'	4	2.46	"
	1-1''	2	2.21	"
	1-2'	4	2.52	"
	1-2'''	4	2.46	"
	2-2'''	2	2.31	"
	2-2'	2	2.50	"
	3-4	4	2.43	"
	1-3	4	2.43	"
III	C..C			
	1-4'	4	2.88	7.0
	1-2''	4	3.16	"
	2-2''	2	3.40	"
	1-3'	4	3.57	"
	2-3'	4	3.69	"
	3-3'	1	4.48	"

Table 2 (Cont'd)

	Terms	Multiplicity	Distances A	a_{ij} 10^4A^2
IV	C-H	14	1.09	23
V	C.H			
	α'-1',1''',2	12	2.29	35
	β'-1,4,3	12	2.27	35
	γ-2	8	2.23	"
	δ'-1,1,4'	6	2.24	"
VI	C..H			
	δ-1	4	3.42	∞
	δ-1''	4	3.93	35
	δ-2''	4	3.27	35
	δ-3	4	2.97	"
	α-4	4	3.42	"
	α-4'	4	3.96	"
	α-1''	4	3.04	∞
	α-2'	4	3.33	"
	α-2''	4	3.41	"
	α-3	4	3.07	"
	α-3'	4	4.55	"
	β-4'	4	3.44	35
	β-1'	4	3.44	∞

Table 2 (Cont'd)

Terms	Multiplicity	Distances A	a_{ij} $10^4 A^2$
β-1''	4	4.13	35
β-1'''	4	3.20	"
β-2'''	4	3.06	∞
β-2''	4	4.40	"
β-2'	4	3.35	"
β-3'	4	4.44	"
γ_1-4	4	3.42	"
γ_1-1	4	2.72	35
γ_1-1'	4	4.13	∞
γ_1-2'	4	4.54	"
γ_1-3'	2	5.37	"
γ_2-1'	4	4.44	"
γ_2-2'	4	4.20	"
γ_2-3'	2	4.90	"
γ_2-4	4	3.42	"

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[1] α-Hydrogen bonded to 1
β- " " " 2
γ_1-Hydrogen (above plane 232''') bonded to 3
γ_2- " (below " ") " " "
δ-Hydrogen bonded to 4.

From the above considerations we conclude that the proposed structural formula is consistent with the electron diffraction pattern. A curve was calculated (not shown) based on model 4 with the C-C bonded distances varied in a manner indicated by the bond strain calculation (see later text) without changing the average distance. No significant effect on the appearance of the curve was observed. No further attempt at differentiating the C-C bond lengths was made in view of the large number of parameters involved.

In the case of norbornane the range of acceptability (fig. 4) appears to be larger than for the cage. The parameters used in calculating the models are listed in Table 2, and the calculated curves are shown in fig. 5. Curves B, C, G and J are clearly unacceptable because of the shape of maximum 6 and/or 8 (G and J also failed in the three-fold comparison of minima 7, 8 and 9), while curves A, F and H are at the limit of the range of acceptability. Curve E was adjudged to represent the best model and gives excellent agreement with the visual curve. As in the case of the cage all models within the range of acceptability can be made to give good agreement with the visual curve and no effort was made to resolve the differences in the C-C bond lengths.

Calculations of the expected bond strain due to cross-ring repulsions were made for models within the range of acceptability. If a Hooke's Law potential is assumed for bond stretching and for first neighbor repulsions (the valence deformation forces are assumed negligible), then the force on atom i due to atom j can be expressed as (see Table 5):

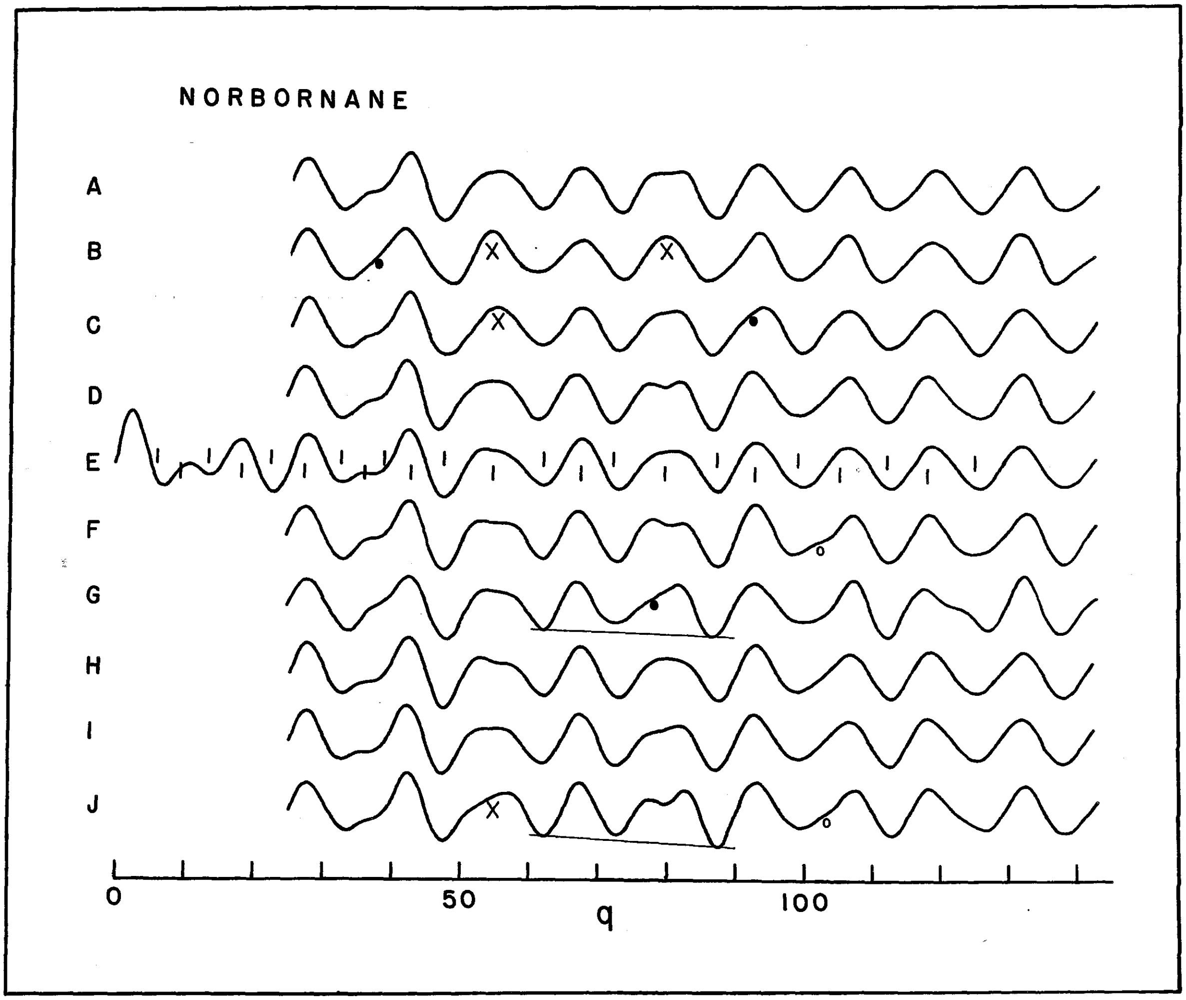

Figure 5

Table 3

Norbornane Parameters of Fig. 5

Model	∡ BCB'	∡ ABA'	$a_{C.C}$	a_{C-H}	$a_{C.H}$	$a_{C..H}$
			$(10^4 A^2)$	$(10^4 A^2)$	$(10^4 A^2)$	$(10^4 A^2)$
A	98.7	104.8	4.5	16.0	41.0	80.0
B	96.3	115.3	"	"	"	"
C	96.3	108.8	"	"	"	"
D	"	105.2	"	"	"	"
E	"	"	10.1	"	"	"
F	"	101.5	4.5	"	"	"
G	"	96.0	4.5	"	"	"
H	95.0	101.7	10.1	"	"	"
I	93.0	105.8	10.1	"	"	"
J	90.5	106.5	4.5	"	"	"
K[1]	90.5	115.8	4.5	"	"	"
L[1]	98.7	113.5	"	"	"	"
M[1]	90.5	97.2	"	"	"	"
N[1]	98.7	95.5	"	"	"	"

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[1] Not illustrated in Fig. 5

Table 4

Interatomic Distances for Norbornane model E

Terms			Multiplicity	Distances A	a_{ij} 10^4A^2
I	C-C		8	1.55	0
II	C...C				
		AC	4	2.39	10.1
		AB'	4	2.45	"
		BB'	1	2.31	"
		AA'	2	2.46	"
III	C...C				
		AA''	2	2.91	"
IV	C-H		12	1.10	16
V	C.H				
		β^1-B	4	2.19	41
		β-A'''	4	2.19	"
		α^1-A'''	4	2.20	"
		α-B	4	2.20	"
		δ^1-B	4	2.22	"
		γ^1-A	4	2.25	"
		γ-C	2	2.25	"
VI	C..H				
		α-A'	4	2.60	80
		δ-A	4	2.66	"
		β-C	4	2.85	"
		β-B'	4	3.18	"
		α-B'	4	3.19	"
		α-A''	4	3.22	"
		γ-B'	2	3.33	"
		α-C	4	3.36	"
		δ-A'	4	3.41	"
		γ-A'''	4	3.43	"
		β-A'	4	3.44	"
		β-A''	4	3.93	"

Table 4 (Cont'd)

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1 α, Bonded to A (on the same side of plane A-A'-A''-A''' as C and B).

β, " " A.

γ, " " B.

δ, " " C.

$$\underset{\sim}{F}_{ij} = F_{T_{ij}} \frac{\underset{\sim}{r}_j - \underset{\sim}{r}_i}{r_{ij}}$$ for bond stretching,

$$\underset{\sim}{F}_{ij} = F_{R'_{ij}} \frac{\underset{\sim}{r}_j - \underset{\sim}{r}_i}{R_{ij}}$$ for repulsion

where

$F_{T_{ij}}$ tension on bond between atoms i and j

$F_{R'_{ij}}$ repulsive force between atoms i and j,

$\underset{\sim}{r}_k$ vector from origin to atom k

$r_{ij} = |\underset{\sim}{r}_i - \underset{\sim}{r}_j|$, bonded, $R_{ij} = |\underset{\sim}{r}_i - \underset{\sim}{r}_j|$, nonbonded, first neighbors.

For equilibrium $\sum_{ij} \underset{\sim}{F}_{ij} = 0$ for all atoms i. In the actual calculations all vectors were resolved into Cartesian coordinates. The scheme followed was to solve the equations for the magnitudes of the repulsive and tensile forces for each model, as is possible because $\underline{r}_k$ is known from the parameters of the model, rather than to solve for the equilibrium configuration on the basis of assumed force constant values. However, there are more unknowns than equations. In order to solve these equations, the minimum number of repulsive forces (consistent with Hooke's Law, $F_{R'_{ij}} = k_1(R_{ij} - R_o)$)) (Table 5) were assumed* and the

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* For the cage the results of independent calculations by A.B. and C.W. are listed. C.W. chose the repulsive forces to be equal to $k_1(R_{ij} - R_o)$ whereas A.B. chose slightly different forces in an attempt to accomplish a rough "least square" result. For norbornane $F_{R'_{ij}} = k_1(R_{ij} - R_o)$ was chosen.

Table 5

Summary of Bond Stretching Calculations

Cage (Model 4)

F^1_R	R^o-R_{ij} (A)	Assumed Forces A.B.	Calc. Forces A.B.	Assumed Forces C.W.	Calc. Forces C.W.
1-3	.09		$.098k_1$	$.09k_1$	
1-4	.10	$.086k_1$		$.10k_1$	
1-1''	.31	$.31k_1$		$.31k_1$	
1-2'	.00	0		0	
1-2'''	.06	$.052k_1$		$.06k_1$	
2-2'	.02		$.050k_1$		$.083k_1$
2-2'''	.21		$.193k_1$		$.176k_1$
2-4'	.06	$.052k_1$		$.06k_1$	
3-4	.09	$.098k_1$			$.09k_1$

F^1_T	Calc. Tension A.B.	Calc. Stretch A.B. (A)	Calc. Tension C.W.	Calc. Stretch C.W. (A)
1-1'	$.238k_1$	.018	$.250k_1$	.019
1-1'''	$.340k_1$	.025	$.347k_1$	.026
1-2	$.199k_1$	.015	$.213k_1$	.016
2-3	$.235k_1$	.018	$.216k_1$	.016
2-4	$.219k_1$	.016	$.247k_1$	.019
4-4'	$.258k_1$	.019	$.280k_1$	.021
		Ave. Stretch	.019 A	.020 A
		Stretch + 1.54,	1.559 A	1.560 A

Table 5 (Cont'd)

Norbornane (Model E)

$F_{R'_{ij}}$	R^o-R_{ij}	Assumed Forces	Calc. Forces
A-C	.13	$.13k_1$	
B-B'	.21		$.232k_1$
A-A'	.06		$.080k_1$
A-B'	.07	$.07k_1$	

$F_{T_{ij}}$	Calc. Tensions	Calc. Stretch
A-B	$.229k_1$	.017
B-C	$.309k_1$	.023
A-A'''	$.153k_1$	.011

Ave. Stretch .017 A

Stretch + 1.54 = 1.557 A

1

$$F_{T_{ij}} = k_2 (r_{ij} - r_o)$$

$$F_{R'_{ij}} = k_1 (R_{ij} - R_o)$$

r_o) normal C-C single-bond length

R_o) normal non-bonded distance assuming tetrahedral angle, 2.52 A

k_2) force constant for C-C single-bond stretching, 4 $\frac{\text{md}}{\text{A}}$ (6)

k_1) force constant for C.C repulsion, 0.3 $\frac{\text{md}}{\text{A}}$. (This value is assumed from the bending force constant of ∢C-C-C.) (6)

Table 6

Cage

Max.	Min.	q_o^1	Wt.	q_c/q_o(4b)
	1	6.07		
1		9.86		
	2	14.19		
2		18.33		
	3	22.56		1.004
3		26.72		1.040
	4	31.82		1.014
4		35.14		1.002
	5	38.19		.985
5		42.60	1	.998
	6	47.33	1	1.010
6		50.95		1.022
	7	54.28		1.003
7		58.04		.977
	8	62.40	1	.996
8		66.46	1	1.005
	9	72.47		1.007
9		76.75		
	10	80.17		.998
10		83.22		
	11	87.35	1	1.000
11		91.85	1	1.004
	12	96.49		1.021
12		99.98		
	13	103.07		
13		106.83		1.001
	14	111.93	1	1.002
14		(117.65)		1.004
	15	(124.82)		
15		(132.65)		
		Ave. 7		1.002
		Ave. 22		1.005
		Mean div. 7		.0035
		" " 22		.0088

For "cage" C-C $= 1.56 \times \frac{q_c}{q_o}(4b) = 1.56\ (1.002) = 1.563$

---

[1] Ave. of C.W., A.B. and V.S.

( ) V.S. only

Table 7

Norbornane

Max.	Min.	q_o^1	q_c/q_o(E)	Wt.
	1	6.07		
1		9.46		
	2	13.55		
2		18.38		
	3	22.64	1.014	
3		27.48	1.021	
	4	32.75	1.011	
4		36.12		
	5	38.96		
5		42.92	.996	1
	6	47.77	1.002	1
6		54.91		
	7	62.35	1.002	1
7		67.72	1.004	1
	8	72.47	1.012	1
8		80.07		
	9	87.54	1.002	1
9		92.99	1.003	1
	10	99.21	1.008	
10		105.34	1.011	
	11	112.58	1.004	
11		118.32	1.006	
	12	125.12		
12		128.14		
	Ave. 7	1.003	Ave. div.	.004
	Ave. 14	1.007	Ave. div.	.005

$r_{C-C} = 1.55 \times 1.003 = 1.555$

---

[1] Ave. of C.W., A.B. and V.S.

remaining repulsive and tensile forces calculated. The results of these calculations are listed in Table 5 for cage model 4 and norbornane model D.

The calculated values for the bond lengths in the cage and norbornane are respectively 1.560 A and 1.557 A (Table 5), in surprising agreement with the experimental values of $1.56_3 \pm 0.01$ A (Table 6) and $1.55_5 \pm 0.01$ A (Table 7).

The electron diffraction result (for $\gamma = 0$, fig. 4) indicates that model 3 is the 'best model' for the cage. However, model 4 was chosen to be the best model for consistency both with the electron diffraction result and the above simple calculation.* In the case of norbornane, the best electron diffraction model is consistent with the calculation.

---

* The indication is that by increasing γ, the range of acceptability of $\measuredangle$ 232''' and $\measuredangle$ 242' would expand in the general direction of models 4 and 5. This would presumably push model 4 (with $\gamma > 0$) toward the center of the range of acceptability in three-dimensional shape parameter space. Although the assumptions on which the bond strain calculations are based force $\gamma = 0$, the very approximate nature of these calculations cannot be ignored.

Table 8

The Bond Angles of Cage (4b) and the Corresponding Bond Angles of Norbornane (E)

Cage		Norbornane	
232'''	95°30'	BCB'	96°19
423	102°18'	ABC	99°43'
321	102°18		
124	101°43'	ABA'	105°14'
211'''	104°4'	BAA'''	104°11'
244'	104°4'		
242'	106°29'		
211'	107°43'		
1'11'''	90°		

II. The Molecular Structure of Ferrocene,

Bis-cyclopentadienyl Iron

The discovery of bis-cyclopentadienyl iron by Kealy and Pauson (7) has been followed by preparations of the analogous compounds of several other metals by several investigators. Many of these compounds appear to have the interesting "sandwich" structure postulated by Wilkinson, et al. (8) and confirmed in the case of ferrocene by chemical properties (8), infrared spectrum (8), X-ray diffraction (9), and nuclear magnetic resonance spectrum (10). We felt that an electron diffraction investigation of the vapor would be worth while*, particularly because we could hope to obtain more accurate values for some of the structure parameters.

The ferrocene sample, kindly supplied by Professor Wilkinson, was purified by two vacuum sublimations at 70 to 80°C. Diffraction photographs were made on Kodak 50 plates with the sample heated to 100-150°C using 40 kv electrons and a 10 cm camera distance.

The visual data**, which extended to $q = (10/\pi) s = 120$, were analyzed by the usual methods (5) to give the radial distribution curve (fig. 6). The peaks may be interpreted in terms of a sandwich molecule with D_5 symmetry as follows: 1.06 A, C-H; 1.43 A, C-C; 2.05 A, Fe-C; 2.33 A, C...C (intra-ring); 2.88 A, Fe...H; 3.45-4.03 A, C...C

---

* Since the completion of this investigation, Siebold and Sutton (11) have reported the results of an independent electron diffraction investigation of ferrocene.

** All three observers (K.H., W.C.H. and A.B.) independently examined the plates. The curve of A.B. is not illustrated since it contains several erroneous interpretations due to inexperience. The curve of K.H. was given greatest weight for interpreting the theoretical curves because of his greater experience and because the other observers finally agreed with his interpretations.

Legend for Figure 6

Electron diffraction curves for ferrocene[1]

Theoretical intensity curves to illustrate the range of curves studied. On curve E, the best curve, vertical lines represent the measured ring diameters. For all curves shown, Fe-C is 2.05 A.

Model	C-C	a_{Fe-C}	$a_{C\ldots C}$[3]	C[4]	q/q_o[2]	Mean dev.
A	1.45	0.0010	0.0027	10	1.006	0.0037
B	1.41	0.0010	0.0027	10	1.009	0.0070
C	1.43	0.0010	0.0027	10	1.007	0.0064
D	1.43	0.0010	0.0027			
E	1.43	0.0020	0.0027	10	1.007	0.0046
F	1.43	0.0010	0.0027	0.2		
G	1.43	0.0010	$\left\{\begin{matrix}0.0026\\0.0023\\0.0020\end{matrix}\right\}^{5}$	staggered[6]		
H	1.43	0.0010	$\left\{\begin{matrix}0.0026\\0.0023\\0.0020\end{matrix}\right\}^{5}$	opposed[6]		
J	1.43	0.0010				
K	1.43	0.0010	0.0100	staggered[6]		
L	1.43	0.0010	0.0100	opposed[6]		

---

[1] The meaning and use of the critical marks on the curves are discussed by W. F. Sheehan, Jr. and V. Schomaker, *J. Am. Chem. Soc.* (1952) *74*, 4468-9.

[2] Weights: K.H. 6; W.C.H. 3; A.B. 1

[3] Inter-ring

[4] In the expression $P(\theta) = 1 + C + \cos 5\theta$ (see later text)

[5] See footnote on page 32

[6] For these models the rings were assumed to be vibrating about their equilibrium positions with no rotation.

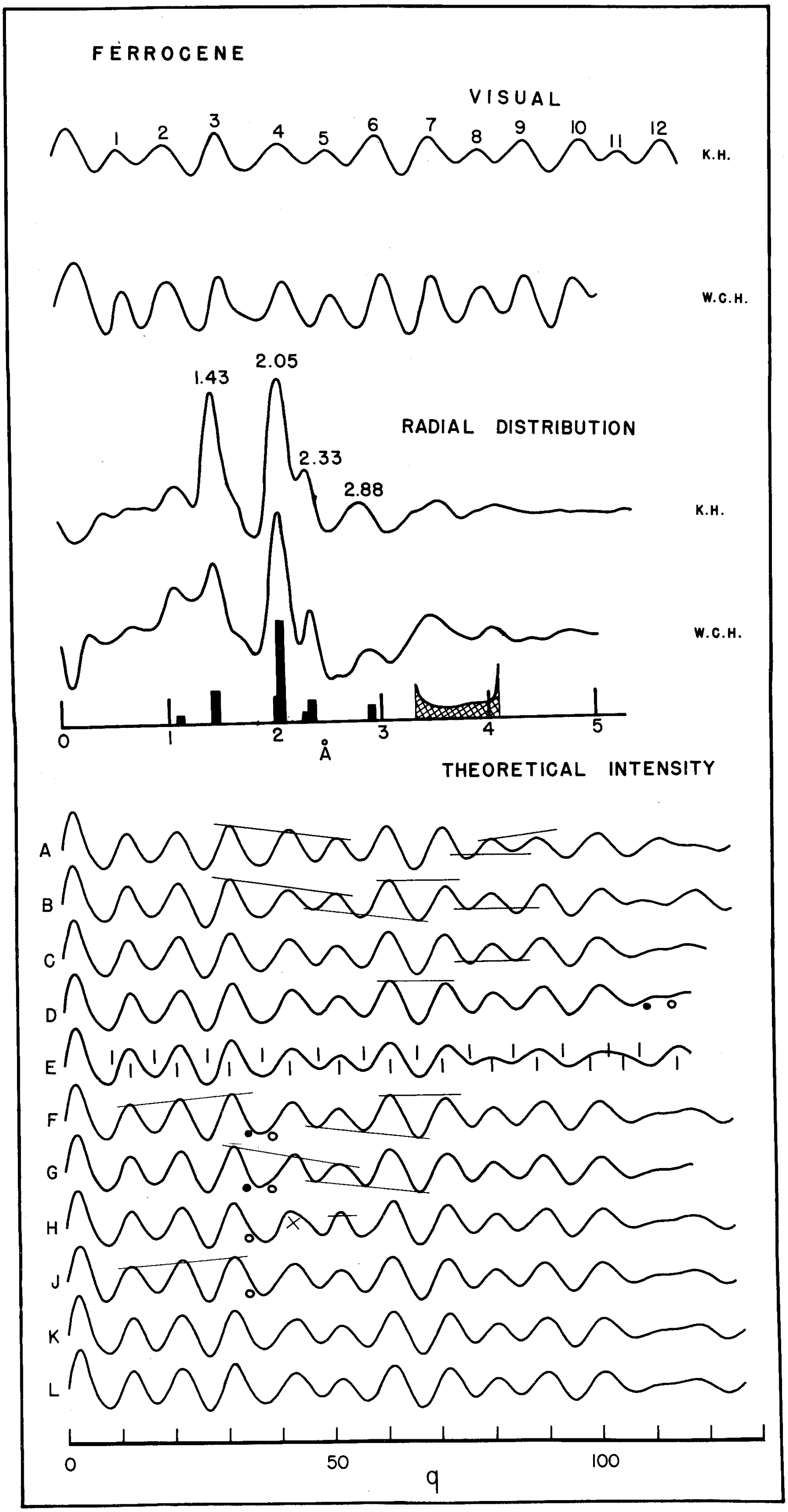
FERROCENE
VISUAL
1
2
3
4
5
6
7
8
9
10
11
12
K.H.
W.C.H.
1.43
2.05
RADIAL DISTRIBUTION
2.33
2.88
K.H.
W.C.H.
0
1
2
3
4
5
Å
THEORETICAL INTENSITY
A
B
C
D
E
F
G
H
J
K
L
0
50
100
q

Figure 6

(inter-ring). The Fe...H peak of the radial distribution curve is consistent with a model in which the hydrogen atoms are in the planes of the rings.

Theoretical intensity curves, some of which are illustrated in fig. 6, were calculated for the following ranges of the structure parameters: 1) $1.40/2.05 \leqslant \text{C-C/Fe-C} \leqslant 1.45/2.05$; 2) $0.0010 \leqslant a_{\text{Fe-C}} = \left(\frac{1}{2}\langle \delta r_{\text{Fe-C}}^2 \rangle - \frac{1}{2}\langle \delta r_{\text{C-C}}^2 \rangle\right) \leqslant 0.0020$. All temperature factor constants other than $a_{\text{Fe-C}}$ and $a_{\text{C...C}}$ (inter-ring), were kept constant and are listed in Table 10. The value of C-H/Fe-C was assumed to be 1.08/2.05. The legend to fig. 6 lists the parameters used for calculating the illustrated curves along with q/q_o values and their mean deviations for several of these curves.

Relative motion of the two rings was investigated by considering models in which the rings were assigned a small vibrational temperature factor constant and allowed to rotate, as well as models in which the inter-ring vibrational temperature factor constants were varied, with no rotation. Quadratic potential functions for both D_{5d} (staggered) and D_{5h} (opposed) equilibrium configurations were investigated. All terms except the H...H terms and the inter-ring C...H terms were included. An effective value of 1.25 for Z_H was used.

The final structure parameters with their estimated limits of error, based on the assumption of a sandwich molecule with D_{5d} symmetry, are summarized in Table 10. The final interatomic distances are illustrated by vertical lines under the radial distribution curve in fig. 6. The shaded area illustrates the spectrum of C...C inter-ring distances for free rotation (not to the same vertical scale). Conclusions concerning relative motion of the rings are discussed in the later text. Table 9 lists q/q_o values for the best model, model E. Fig. 7 illustrates the variation of q/q_o over the range of acceptability for the three observers.

One of the methods used for investigating the relative motion of the two rings was to assume that the probability distribution of angular displacement from the assumed staggered equilibrium position was of the form

$$P(\theta) = 1 + C + \cos 5\theta$$

where θ is the angular displacement from the equilibrium position. Free rotation is therefore represented by $C = \infty$, while a finite value of C represents a non-zero potential barrier. This approximation has the shortcoming of not being capable of representing a large potential barrier. For these models no attempt was made to prove whether the equilibrium configuration is D_{5d} or D_{5h}. For consistency with the crystal structure (9), D_{5d} was assumed. An arbitrary vibrational temperature factor constant $a_{C...C} = 0.0027$ was assigned to the inter-ring C...C distances* and the parameter C was varied from 0 to ∞. Any value of C greater than 5 is compatible with the visual data. The value $C = 5$ corresponds to a potential barrier to rotation of approximately 1/4 kcal/mole**. Therefore the inability of the assumed distribution function to represent large potential barriers is not harmful.

---

* In earlier models, e.g., G and H (fig. 6), separate temperature factor constants were assigned to each of the different inter-ring C...C distances. However, the effect of the different temperature factor constants was seen to be negligible and one temperature factor constant was then assigned to all inter-ring C...C distances.

** $$P(\theta) = 1 + C + \cos 5\theta \approx (1 + C)e^{-\frac{V_0}{2}\frac{\cos 5\theta}{kT}}$$

For $C = 5$, $T = 400^{\circ}K$, $V_0 = 1/4$ kcal/mole

Legend for Table 9

Table of q/q_o

The data of the three investigators were weighted according to their relative experience in measuring and interpreting electron diffraction photographs. The weights to be assigned to the various rings were determined as follows: 1) Inner rings were assigned weight zero because of the relatively large percentage error introduced into q by a small variation in the measured diameter. 2) Extreme outer rings were assigned weight zero because of their weak intensity. 3) Features which would be expected to exhibit a large St. John's error, e.g. highly asymmetric features and extremely broad features, were assigned weight zero. 4) All other features were assigned weight one.

Table 9

max.	min.	$q_{\text{Calc.}}^{*}$	W.H. q/q_o***	K.H. q/q_o	A.B. q/q_o	Ave. q/q_o**	Weight
	1	7.9	0.845	0.946	0.959		0
1		12.0	.966	1.009	1.001		0
	2	16.5	1.003	1.041	.996		0
2		21.4	1.028	1.038	1.030		0
	3	26.5	.985	1.018	.998	1.006	1
3		31.2	1.007	1.017	1.027	1.015	1
	4	36.9	1.001	1.023	.997		0
4		42.6	1.010	1.008	1.022	1.010	1
	5	47.7	.999	1.004	1.015		0
5		51.2	.992	1.002	1.001	.999	1
	6	55.8	.984	1.013	.992		0
6		60.9	.994	1.003	1.005	1.001	1
	7	66.6	1.006	1.014	1.009	1.011	1
7		71.6	1.010	1.014	1.022	1.014	1
	8	76.2	1.007	1.005	1.008		0
8		80.0	.997	1.005	1.003	1.002	1
	9	83.5	.992	1.004	.988		0
9		88.7	1.005	1.005	1.003	1.005	1
	10	93.9	1.012	1.007		1.009	1
10		101.0	.997	.990	1.029		0
	11	109.3		1.018			0
11		115.0		1.005			0
Weighted Average			1.002	1.009	1.010	1.007	
Mean Deviation			.0078	.0051	.0091	.0046	

* From the best curve, curve E

** Data averaged with the following weights:

W.H. 3
K.H. 6
A.B. 1

*** $\lambda = 0.06176$ A
$\ell = 9.627$ cm

Figure 7

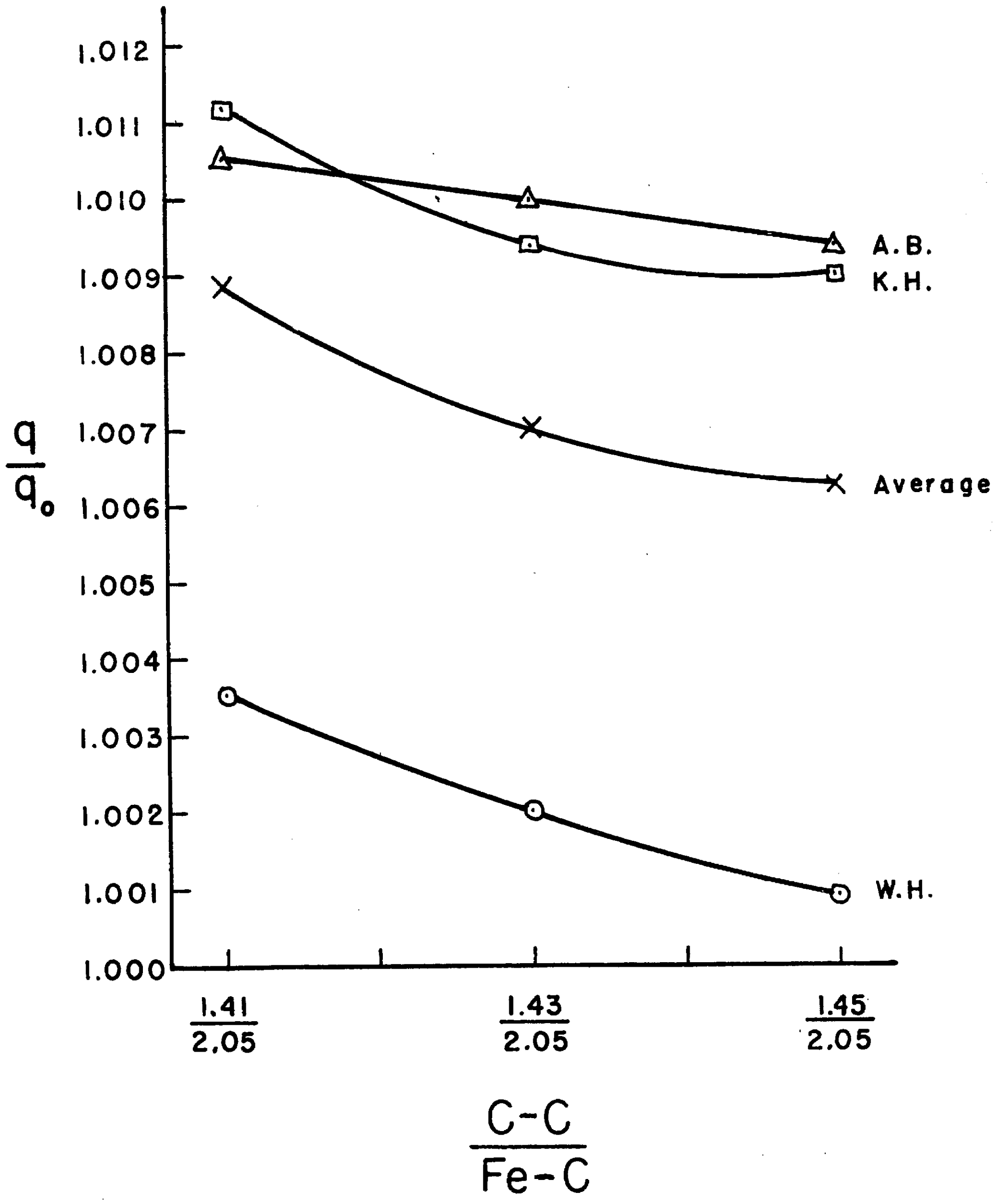
q/q₀
1.012
1.011
1.010
1.009
1.008
1.007
1.006
1.005
1.004
1.003
1.002
1.001
1.000
1.41/2.05
1.43/2.05
1.45/2.05
C-C/Fe-C
A.B.
K.H.
Average
W.H.

Table 10

Final Results

	Distance	Limit of Error	a_{ij}
Fe-C	2.064 A	0.013 A	0.0020
C-C	1.440 A	0.029 A	0
C-H	1.087 A*	0.007 A	0.0015**
Fe...H	2.847 A	0.039 A	0.0035**
C...C (intra-ring)	2.330 A	0.038 A	0.0010**
Distance between rings	3.32 A	0.06 A	

The value of Fe-C is equal to the assumed value of 2.05 A multiplied by $\overline{q/q_o}$ (1.007) for the best curve (curve E). This value, 2.064 A, is uncertain due to uncertainties in the value of $\overline{q/q_o}$ resulting from; 1) uncertainty in $\overline{q/q_o}$ for the best curve; 2) instrumental errors; 3) variations in $\overline{q/q_o}$ over the range of acceptable curves (fig. 7). The resultant uncertainty in Fe-C due to effects 1) and 2) was assumed to be 0.01 A. The uncertainty due to 3) is 0.13%. The net uncertainty in the value of Fe-C is therefore the sum of these effects $\left(2.05\frac{0.13}{100} + 0.01\right)$.

$$C-C = Fe\text{-}C\left(\frac{C-C}{Fe\text{-}C}\right)_{\text{Best Curve}}$$

An uncertainty in C-C arises because of the uncertainties in Fe-C (including instrumental errors) and in C-C/Fe-C (1.43/2.05 ± 0.02/2.05).

$$C\text{-}C = 2.064\ (1.43/2.05) \pm \left\{0.013\ (1.43/2.05) + 2.064\ (0.02/2.05)\right\}$$

---

* Assumed ratio C-H/Fe-C = 1.08/2.05

** Assumed

The other method for investigating the relative motion of the two rings was to consider models with no internal rotation and to vary the inter-ring C...C temperature factor constants. The vibrational temperature factor constant was varied over the range $0.0025 \leqslant a_{C...C} \leqslant \infty$ for models with both D_{5d} and D_{5h} symmetry. Satisfactory agreement with the visual data was obtained for $0.0100 \leqslant a_{C...C} \leqslant 0.0200$ for both symmetries.

Comparison of curve J (Fig. 6), in which the inter-ring C...C terms are omitted, i.e., $a_{C...C} = \infty$, with the visual curve indicates that the desired effect is to have the inter-ring C...C terms die out rapidly. The necessary result is obtained with models having either a small barrier to rotation or models having a moderately large inter-ring C...C temperature factor constant. Our electron diffraction investigation is incapable of distinguishing between these two models.

Curves A, B, C and E (fig. 6) illustrate the ranges of the ratio C-C/Fe-C and a_{Fe-C} investigated. For $q < 70$ only C-C/Fe-C is important, but beyond $q = 70$, reasonable variations of both C-C/Fe-C and a_{Fe-C} affect the curves.

These curves (as well as the others illustrated) may be interpreted, assisted by the critical marks, as follows.

Visual observations showed minimum 4 to be asymmetric in a manner which is represented satisfactorily by curves C, D, E, L and K*.

---

* This feature is exaggerated on the visual curve of W.C.H. and does not represent a basic disagreement in interpretation. The visual observations are best represented by the curve of K.H.

Increasing the ratio (curve A) gives a poor fit for maximum 5 which was observed to be a weak, narrow maximum. Increasing the ratio also destroys the fit in the relationship between maxima 8 and 9. Maximum 4 was observed to be equal to the average of maxima 3 and 5. Curves for C-C/Fe-C $= 1.43/2.05 \pm 0.02/2.05$ are consistent with these features. The feature at about $q = 100$ was judged to have the appearance of a doubled maximum or an extremely broad maximum. Curves B and E represent this satisfactorily. This feature would be made acceptable on curves D, L and K by increasing a_{Fe-C}, as illustrated by comparison of curves C and D. Of all the curves calculated, curve E was judged to represent the best fit with the visual data. The best value for the ratio was judged to be 1.43/2.05 while the ratios 1.41/2.05 and 1.45/2.05 were judged to lie on the border of the acceptable range. Although curves were not calculated for all values of the ratio C-C/Fe-C nor for all temperature factor constants, interpolations were made to determine the appearance of these curves.

The failure of the Born Approximation (12) would manifest itself by a broadening of the Fe-C peak of the radial distribution curve. The expected split is calculated (12c) to be 0.06 A, which corresponds to an increase of 0.0005 in the derived value of a_{Fe-C}. The value of the intra-ring $a_{C...C}$ was assumed to be 0.0010 from considerations of the widths of the radial distribution peaks corresponding to C...C and C-C. The derived value of a_{Fe-C} will depend upon the assumed value for a_{C-C}.

X-ray analysis of the ferrocene crystal has yielded the following average results (9d): Fe-C $= 2.045$ A, $\sigma = 0.024$ A; C-C $= 1.403$ A, $\sigma = 0.040$ A. Our results (Table 10) are in fairly good agreement with these X-ray results but they do seem to indicate a considerably larger molecule. Siebold and Sutton (11) have reported an electron diffraction result of Fe-C $= 2.03 \pm 0.02$ A and C-C $= 1.43 \pm 0.03$ A.

A C-C bond with length 1.440 A has 23% double bond character (13) which is less than the 40% double bond character which would be predicted from a model in which each ring has two C-C double bonds and one Fe-C bond, resonating among the five positions. Pauling's formula (14), $R(1) - R(n) = 0.300 \log n$, was used in order to determine the bond number, n, for the Fe-C bond. In this formula, R(n) is the radius of the atom in a bond with bond number n and R(1) is the single bond radius. If the single bond radii of Fe and C are taken as 1.165 A and 0.771 A (14), respectively, then Pauling's formula gives $n = 0.61$ for a Fe-C bond of 2.064 A. Therefore there are 1.22 electrons associated with each Fe-C bond and 2.46 electrons associated with each C-C bond. The sum of the electrons associated with each carbon atom is therefore 8.14, taking 2.00 electrons for the C-H bond, in satisfactory agreement with the expected value of 8.00.

Each carbon atom may be said to contribute 3.46 $(1.23+1.23+1.00)$ electrons to the C-C and C-H bonding. Therefore each of the ten carbon atoms has 0.54 electrons available to contribute to the Fe-C bonding. Since the total Fe-C bonds contain 12.2 electrons of which 5.4 are contributed by the carbon atoms, then the iron atom must contribute 6.8 electrons to the bonding in the molecule. This is not inconsistent with the fact that an iron atom has eight electrons more than a noble gas structure.

III. The Crystal Structure of Cyclopentadienyl Manganese Tricarbonyl

The existence of sandwich molecules was first postulated by Wilkinson, et al. (8) in 1952 on the basis of chemical evidence which indicated that Kealy and Pauson's (7) proposed ionic structure for ferrocene, $(C_5H_5)_2Fe$, was incorrect. The sandwich structure of ferrocene has since been confirmed by X-ray and electron diffraction studies (9, 11, 15) and evidence of sandwich bonds in other molecules has been presented (16, 17, 18).

Since 1951 bis-cyclopentadienyl derivatives of many of the transition metals have been prepared. The preparations of a number of cyclopentadienyl carbonyl compounds of the transition metals and some related nitrosyl derivatives have also been reported (19). In these compounds, among which are $C_5H_5Mn(CO)_3$ and C_5H_5NiNO, the metal atom is said to be bonded to the cyclopentadienyl ring by a "sandwich bond" (19).

A molecular orbital treatment of sandwich molecules indicates that a stable compound will result if the central metal atom is surrounded by eighteen electrons, a rare gas configuration (20). Each cyclopentadienyl ring is assumed to contribute five electrons*. In bis-cyclopentadienyl manganese the central manganese atom is surrounded by only seventeen electrons. Replacement of one ring by three carbonyl groups will increase this number to eighteen, giving a more stable structure, if it is assumed that each carbonyl group contributes two electrons.

---

* Piper, et al. (19) suggest that in mixed cyclopentadienyl carbonyl and nitrosyl compounds the ring contributes one electron to the central atom which then shares fourteen electrons. This view is generally not now accepted (20).

In order to obtain more information relevant to these considerations, a structure investigation of cyclopentadienyl manganese tricarbonyl was made. This compound was treated as a heavy-atom problem.

Cyclopentadienyl manganese tricarbonyl, $C_5H_5Mn(CO)_3$, can be prepared by the action of carbon monoxide under pressure on the mixture resulting from the reaction of sodium cyclopentadienide and manganous bromide (19). Fischer has prepared this compound by reacting pressurized carbon monoxide with manganocene (21). The product may be purified by sublimation in vacuo, and deposits as yellow crystals.

The sample used in this investigation was prepared and supplied by Professor Wilkinson. The crystals used were irregular in shape with a maximum linear dimension of about 0.3 mm. Because of their volatility the crystals were mounted in lithium borate glass capillaries.

Laue and oscillation photographs were used for orienting the crystals. The Laue symmetry was found to be C_{2h}. Equi-inclination Weissenberg pictures were taken, using CuK_α radiation, about the $\underline{b}$ axis and the [102] axis. Intensities on the multiple-film photographs were estimated by visual comparison with an intensity strip and the two sets of data were correlated after application of the Lorentz and polarization factors. About 900 reflections were observed.

The only systematic absences were

$h\,0\,\ell$	h odd
$0\,k\,0$	k odd.

These data indicate the space group to be P_{2_1}/a. The unit-cell parameters, as obtained from Straumanis-type single crystal rotation photographs, are

$$a = 11.99 \pm 0.028 \text{ A}$$

$$b = 7.07 \pm 0.030 \text{ A}$$

$$c = 10.93 \pm 0.023 \text{ A}$$

$$\beta = 117^{\circ}48' \pm 10'$$

The parameters were refined and the standard deviations calculated by least squares. On the basis of four molecules per unit cell, one per asymmetric unit, the calculated density is 1.654 g/cc.

The reflections with $h + k$ odd are, in general, much weaker than those with $h + k$ even. This datum indicates that the position of the manganese atom is such that it makes a small contribution to all $h + k$ odd reflections. The trigonometric part of the manganese contribution to these reflections is $\sin 2\pi(hx + \ell z) \sin 2\pi(ky)$. Therefore, in order that the manganese contribution to all $h + k$ odd reflections be negligible, either y is 0 or x and z are 0. The values $x = z = 0$ were tentatively rejected on the basis of packing arguments. In order to determine the x and z parameters for manganese, an $h0\ell$ Patterson projection (fig. 8)[*] was calculated using Beevers-Lipson strips. The strong peak at $x = 0.080$, $z = 0.526$ can only be a Mn-Mn interaction. This gives the manganese parameters as $z = 0.263$ and $x =$ either 0.040 or 0.290 since in projection a two-fold screw-axis cannot be distinguished from a center of symmetry. Three-dimensional structure factor calculations show

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[*] In this and in other figures, negative contours are omitted.

HOL Patterson Projection

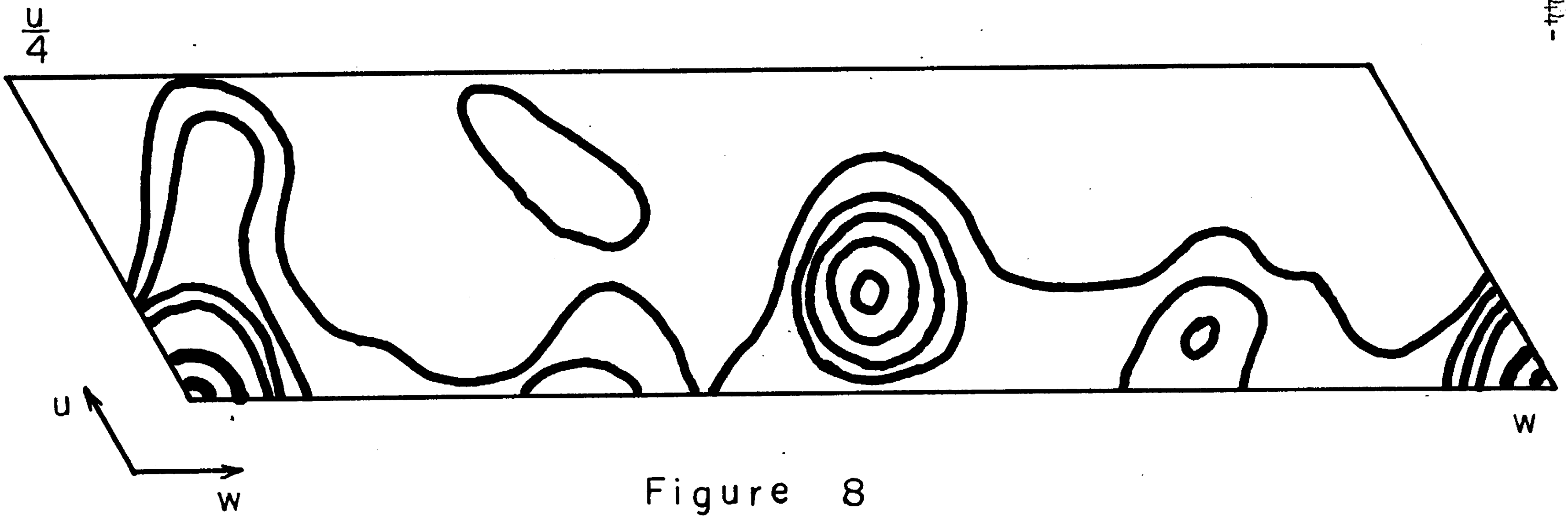

Figure 8

$x = 0.290$ to be consistent with, and $x = 0.040$ to be inconsistent with, the observed data.

An electron density projection onto (010), calculated from the $h0\ell$ reflections using signs as determined by the manganese atoms, did not give a clear indication of the structure. Therefore, three-dimensional methods were employed. In order to reduce the calculating time, the IBM "M-card" system was used. A Fourier synthesis was calculated using only $h + k$ even reflections with signs determined by the manganese. The omission of $h + k$ odd data places a false mirror plane at $y = 0$, leading to a doubling of the number of peaks.

From this Fourier synthesis parameters for the eight carbon atoms and the three oxygen atoms were obtained. Structure factor calculations were made using McWeeny form factors for carbon and oxygen and Thomas-Fermi scattering factors for manganese. Isotropic temperature and scale factors were calculated by Wilson's method. These parameters were then refined using $h0\ell$ and $0k\ell$ Fourier projections (figs. 9 and 10).

These data were further refined by calculating a Fourier synthesis using all reflections for which the sign could be reasonably assigned from the structure factor calculations. Table 12 lists the atomic parameters and R factor at several stages in the refinement.

A difference Fourier synthesis (F_o-F_c synthesis) was calculated. Anisotropic temperature factors were indicated and were estimated by the method of Leung, Marsh and Schomaker (22). The atom shifts were not calculated from the difference Fourier synthesis because they were indicated to be small.

Calculations of structure factors using these anisotropic temperature factors and least squares refinements of the atomic positions were

HOL Fourier Projection

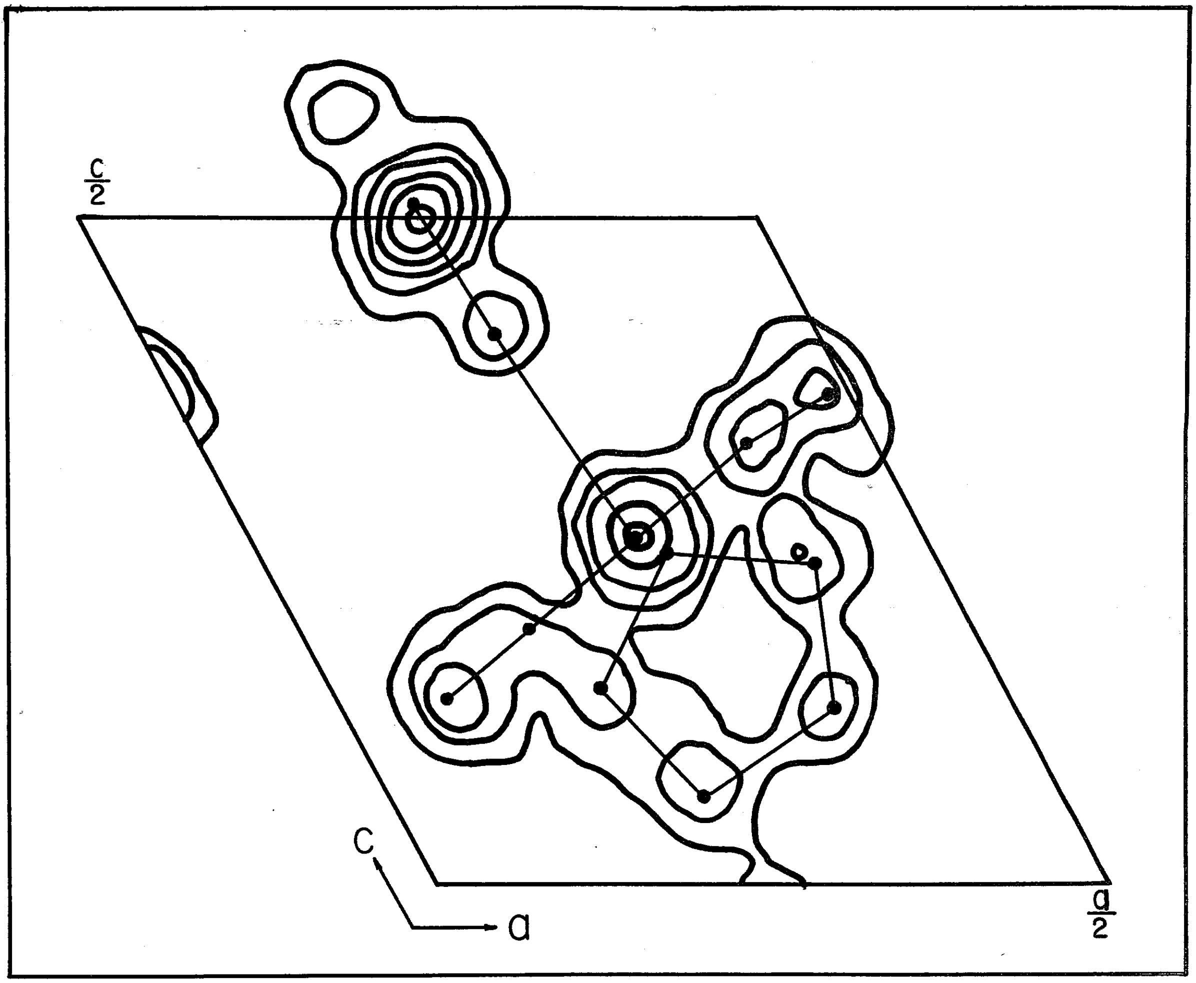

Figure 9

OKL Fourier Projection

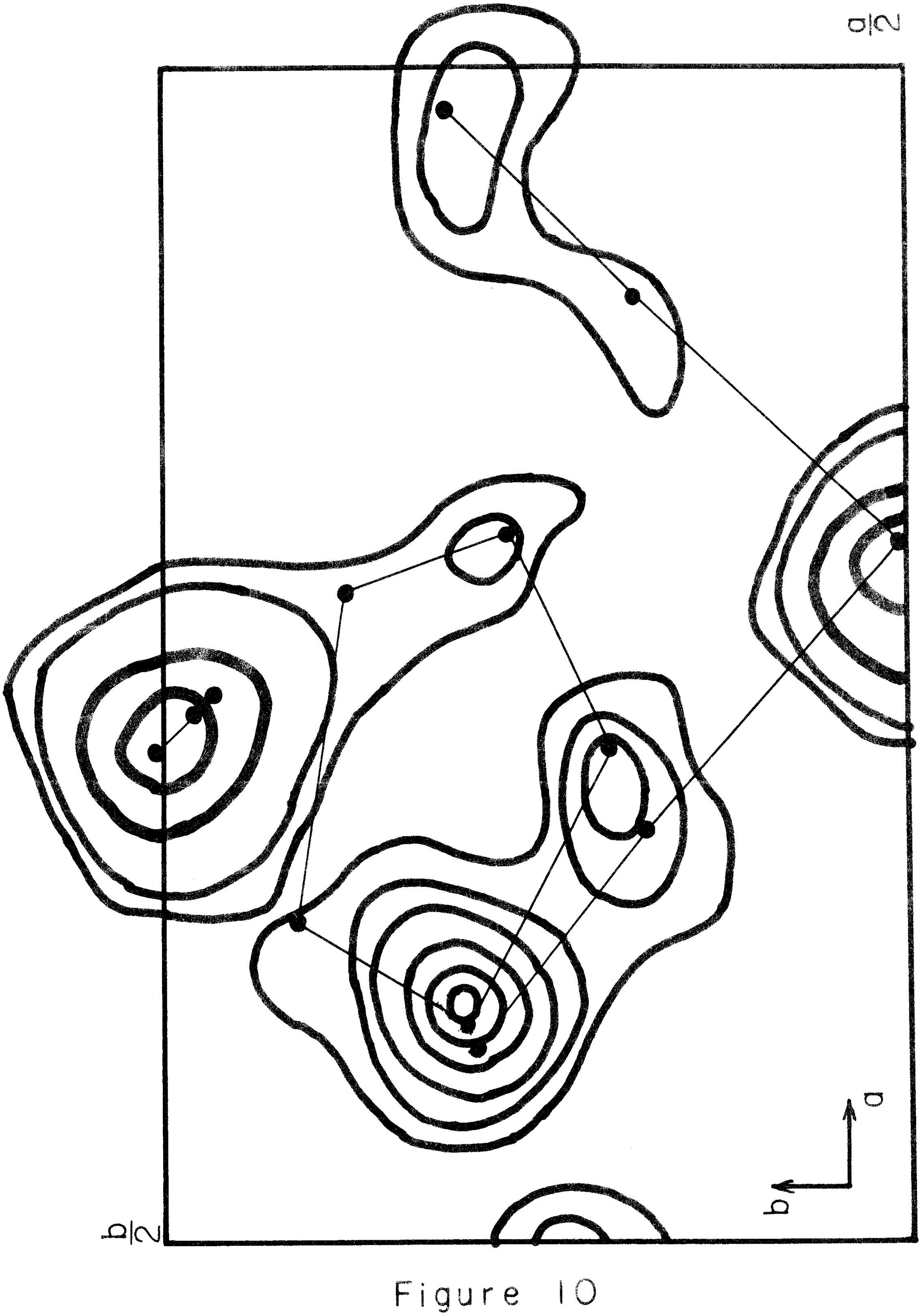

Figure 10

made on the Datatron computer. The program used was written by Pasternak and revised by Marsh and Nathan*. Weights were assigned according to

$$\sqrt{w} = \frac{1}{F_o} \qquad F_o \geqslant 4F_{min}$$

$$\sqrt{w} = \frac{1}{\sqrt{F_o \cdot 4F_{min.}}} \qquad F_o \leqslant 4F_{min}$$

$$\sqrt{w} = 0 \qquad \text{unobserved reflections.}$$

Hydrogen atom contributions to the structure factors were included with parameters calculated by assuming they were in the plane of the cyclopentadienyl ring with an effective C-H distance of 0.95 A.

After two refinements, another difference Fourier synthesis was calculated in order to check the temperature factors. Only minor changes in the temperature factors were indicated; these were made, and three more least square refinements were calculated. In Tables 11, 12 and 13 there are listed, respectively, the final anisotropic temperature factors for all atoms, the final atomic positional parameters** with their standard deviations and the calculated interatomic distances and angles along with their standard deviations calculated from the least squares treatment (see later text). The interatomic distances are also given in fig. 11, which shows a projection of one molecule onto the <u>ac</u> plane. The final R factor

---

* This program takes into account the symmetry of the space group in applying the anisotropic temperature factors.

** In all refinements except the last, the atom shifts were calculated using only the diagonal terms in the normal equations. The final shifts were calculated using an approximation for the xz off-diagonal terms in the complete matrix. These terms were assumed to be equal to cosβ times the square root of the product of the corresponding x and z diagonal terms.

Table 11a

Anisotropic Temperature Factors

Atom	Directions		
	∥ axis of ring	⊥ axis of ring	
Mn	0.360	0.358	0.358
	∥ direction of bond	⊥ direction of bond	
O_1	0.407	0.407*	0.463**
O_2	.374	.462	.423
O_3	.368	.445	.445
C_1	.346	.364	.386
C_2	.342	.364	.402
C_3	.329	.382	.417
	∥ tangent to ring	⊥ plane of ring	∥ radius of ring
Ring C***	0.409	0.375	0.376

---

[*] The values in this column are for a direction described by a line ⊥ the Mn-C-O bond and lying in the plane containing the Mn, C and O and bisecting the opposite C-Mn-C angle.

[**] The values in this column are for a direction perpendicular to each of the other two.

[***] All five ring carbons were assumed to be equivalent and their anisotropic temperature factors were averaged.

Table 11b

Table of Anisotropic Temperature Factor Coefficients

$$T^{*}_{\text{total}} = e^{-0.359\ \sin^2\theta}\, e^{-(\alpha h^2 + \beta k^2 + \gamma \ell^2 + \delta h \ell + \epsilon h k + \eta \ell k)}$$

	α	β	γ	ϵ	δ	η
Mn	-.0001	-.0001	.0000	.0000	-.0001	.0000
O_1	.0023	.0052	.0055	-.0001	.0025	.0001
O_2	.0029	.0066	.0037	.0064	.0030	.0033
O_3	.0041	.0095	.0015	.0000	.0042	.0000
C_1	-.0002	-.0004	.0012	-.0013	-.0002	-.0007
C_2	-.0003	-.0006	.0019	.0015	-.0004	.0009
C_3	.0028	.0025	-.0007	.0000	.0028	.0000
C_4	.0012	.0033	.0015	.0008	.0004	-.0019
C_5	.0020	.0021	.0022	-.0012	.0033	-.0013
C_6	.0018	.0026	.0010	.0017	.0008	-.0002
C_7	.0011	.0030	.0023	-.0011	.0020	-.0026
C_8	.0024	.0018	.0014	.0004	.0026	.0002

The values of the coefficients refer to the parameters listed in Table 12.

---

* $0.359 \sin^2\theta = 0.0171\, h^2 + 0.0407\, k^2 + 0.0210\, \ell^2 + 0.0179\, h\ell$

Table 12

Atomic Positional Parameters

After refinement using projections

	x	y	z
Mn	.290	.000	.263
O_1	.477	.295	.372
O_2	.092	.295	.142
O_3	.250	.000	.500
C_1	.410	.191	.340
C_2	.162	.192	.185
C_3	.263	.000	.413
C_4	.400	-.210	.248
C_5	.360	-.090	.133
C_6	.235	-.125	.074
C_7	.197	-.250	.149
C_8	.306	-.323	.258

R = 25.1

After first F_o-F_c synthesis

	x	y	z
Mn	.290	.004	.265
O_1	.475	.294	.378
O_2	.088	.293	.142
O_3	.262	-.017	.512
C_1	.402	.185	.337
C_2	.165	.175	.192
C_3	.273	-.002	.422
C_4	.398	-.211	.243
C_5	.353	-.097	.128
C_6	.228	-.123	.065
C_7	.197	-.244	.143
C_8	.298	-.300	.253

R = 20.0

Table 12 (Cont'd)

Final parameters

	x	y	z	σ
Mn	.2877	.0075	.2629	0.003 A
O_1	.479	.308	.380	.016
O_2	.083	.289	.146	.016
O_3	.264	-.033	.516	.016
C_1	.399	.185	.330	.021
C_2	.167	.178	.194	.021
C_3	.267	-.020	.417	.021
C_4	.414	-.199	.246	.023
C_5	.357	-.093	.130	.023
C_6	.227	-.115	.060	.023
C_7	.200	-.233	.139	.023
C_8	.301	-.295	.251	.023

$R = 15.6$

Table 13

Calculated Distances and Angles

		σ		
Mn-C_1	1.73 A	.022 A	∢ C_1-Mn-C_2	91.3°
Mn-C_2	1.76	.022	∢ C_2-Mn-C_3	92.6°
Mn-C_3	1.82	.022	∢ C_3-Mn-C_1	93.5°
Mn-O_1	2.95	.017	∢ O_1-Mn-O_2	90.1°
Mn-O_2	2.95	.017	∢ O_2-Mn-O_3	91.7°
Mn-O_3	2.93	.017	∢ O_3-Mn-O_1	95.4°
C_1-O_1	1.22	.027	∢ Mn-C_1-O_1	179.0°
C_2-O_2	1.19	.027	∢ Mn-C_2-O_2	177.8°
C_3-O_3	1.11	.027	∢ Mn-C_3-O_3	174.8°
Mn-C_4	2.17	.024	∢ C_4-C_5-C_6	113.6°
Mn-C_5	2.11	.024	∢ C_5-C_6-C_7	104.9°
Mn-C_6	2.17	.024	∢ C_6-C_7-C_8	113.9°
Mn-C_7	2.13	.024	∢ C_7-C_8-C_4	105.1°
Mn-C_8	2.15	.024	∢ C_8-C_4-C_5	102.3°
C_4-C_5	1.35	.033	Total	539.8°
C_5-C_6	1.39	.033		
C_6-C_7	1.34	.033		
C_7-C_8	1.34	.033		
C_8-C_4	1.54	.033		

		Mean deviation
Ave. Mn-C (Ring)	2.146	.024
Ave. C-C	1.391	.06
Ave. Mn-C	1.770	.033
C-O	1.173	.042

Interatomic Distances

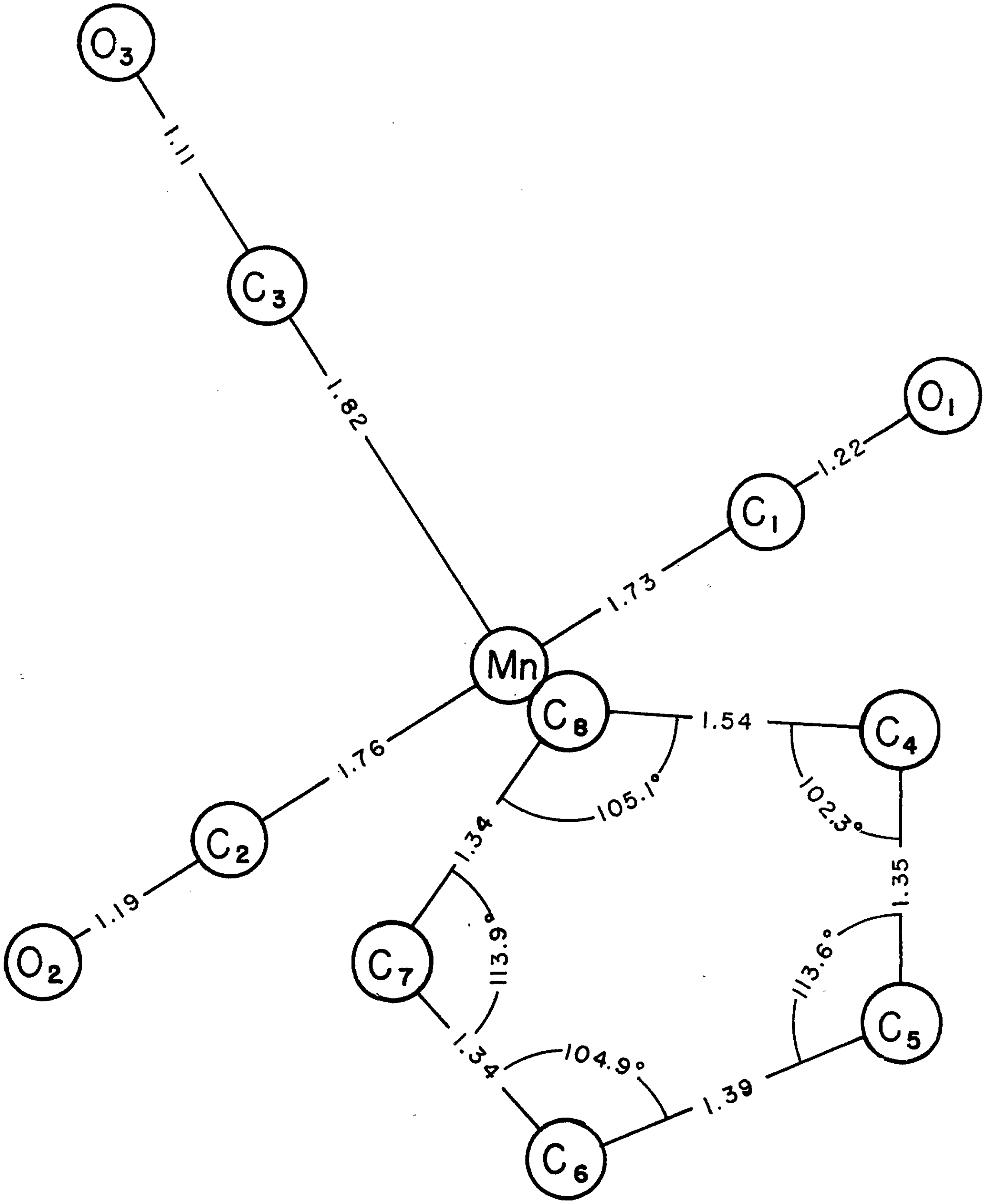

Figure 11

for all reflections is 15.6. For h + k odd reflections R is 21.0 and for h + k even reflections R is 14.3. The observed and calculated structure factors are listed in the appendix.

Piper, et al. (19) propose that $C_5H_5Mn(CO)_3$ exists as a monomer, in contrast to $C_5H_5W(CO)_6WC_5H_5$ which is presumed to be a dimeric "double decker sandwich". Shoemaker and Wilson (18) have recently shown that $C_5H_5Mo(CO)_3$ exists as a weakly-bonded dimer in the crystal with a Mo-Mo distance of 3.22 A. The present investigation confirms Piper's hypothesis for $C_5H_5Mn(CO)_3$: The molecule is a monomer. The shortest Mn-Mn distance is 6.66 A.

The calculated angles indicate that the $Mn(CO)_3$ part of the molecule has nearly C_{3v} symmetry. The C_5H_5 ring is planar, the greatest distance between a carbon atom and the best least-squares plane being 0.016 A. The average C-C distance in the ring is 1.391 A, with a mean deviation of 0.06 A. The angle between the line joining the centroid of the ring with the manganese atom and the line joining the centroid of the oxygen atoms with the manganese atom is 178.0°.

The intermolecular distances, illustrated in figs. 12 and 13, are close to those calculated from the sum of the van der Waals radii of the various atoms. Fig. 12 is a projection of the contents of one unit cell onto the <u>ac</u> plane while fig. 13, a projection along <u>a</u>, illustrates the relation among molecules lying in a plane parallel to the <u>bc</u> plane.

The standard deviations in the atomic positions were calculated from the least squares treatment using the relation (23)

$$\sigma^2 = \frac{\Sigma w v^2}{s - m} \frac{1}{Dq}$$

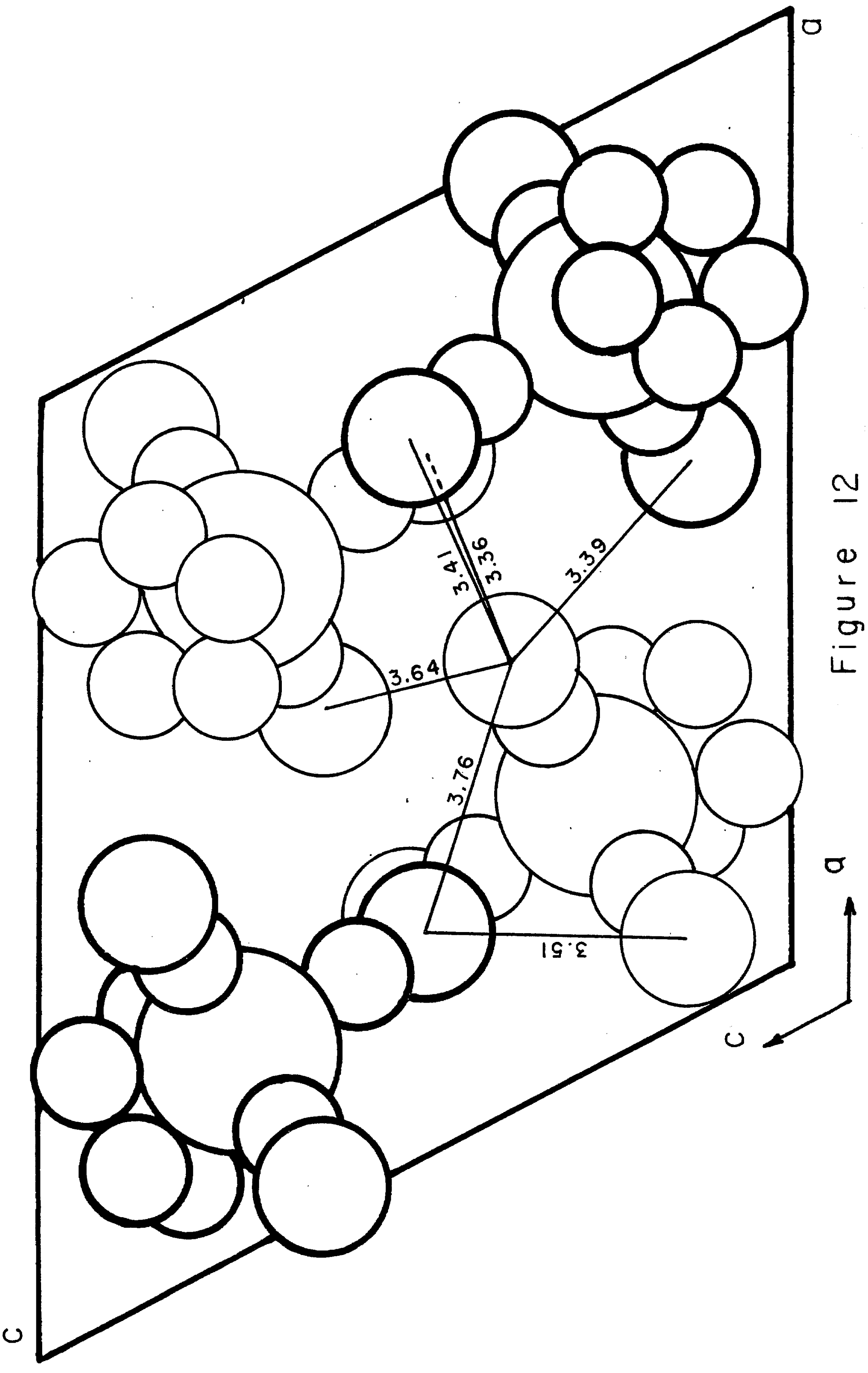

Figure 12

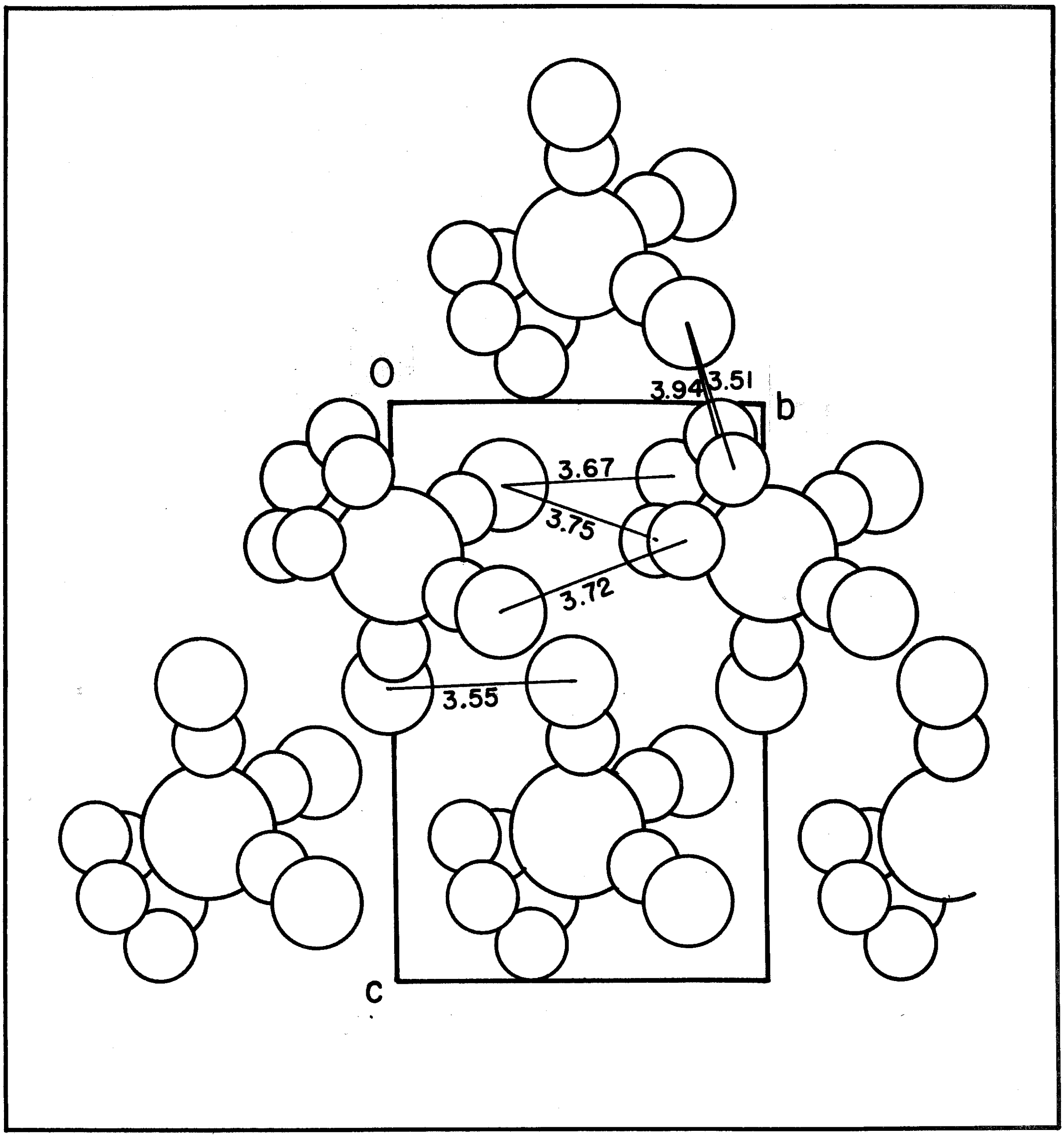

Figure 13

where	$\Sigma w v^2$	is the weighted sum of squares of the residuals,
	s	is the number of observations,
	m	is the number of variables,
	Dq	is the corresponding diagonal term in the normal equation matrix.

The values of σ along the three axes for each atom were averaged and the standard deviations in the bond lengths were calculated as the square root of the sums of the squares of the standard deviations in the positions of the atoms at the ends of the bond.

The difference Fourier synthesis indicates that the ring has a large amplitude of rotatory motion about its axis and a smaller amplitude of out of plane motion in a direction perpendicular to the Mn-C bond. Therefore the temperature factors for the ring carbon atoms have a large anisotropic component along a direction tangent to the ring. The indication is that the carbonyl groups have a greater amplitude of vibration in directions perpendicular to the Mn-C-O bond than in the direction parallel to the Mn-C-O bond.

For purposes of discussing the packing of the molecules, they may be roughly approximated by spheres centered at (1/4, 1/4, 0), (3/4, 1/4, 1/2), (1/4, 3/4, 1/2) and (3/4, 3/4, 0). If the origin is moved to (1/4, 1/4, 0), these coordinates become (0, 0, 0), (1/2, 0, 1/2), (0, 1/2, 1/2) and (1/2, 1/2, 0) and the structure is face centered monoclinic. A face centered cubic structure (i.e., cubic closest packing) may be described in terms of a face centered monoclinic unit cell. If the three cubic axes are called $\underset{\sim}{a_1}$, $\underset{\sim}{a_2}$, $\underset{\sim}{a_3}$, then the monoclinic axes may be taken as

$$\underset{\sim}{a} = \underset{\sim}{a_1} + 1/2\,\underset{\sim}{a_2} + 1/2\,\underset{\sim}{a_3}$$

$$\underset{\sim}{c} = -\underset{\sim}{a_1} + 1/2\,\underset{\sim}{a_2} + 1/2\,\underset{\sim}{a_3}$$

$$\underset{\sim}{b} = 1/2\,\underset{\sim}{a_2} - 1/2\,\underset{\sim}{a_3}$$

For this monoclinic description $a = c$, $\beta = 109^{\circ}28'$ and $b/a = 0.58$. In the actual unit cell $a = 1.10c$, $\beta = 117^{\circ}48'$ and $b/a = 0.59$. Therefore the packing of the cyclopentadienyl manganese tricarbonyl molecules approximates a distorted cubic closest packed array of spherical molecules.

Each oxygen atom is in van der Waals contact with six other oxygen atoms in adjacent molecules. However, O_3 is in contact with the three oxygen atoms in another molecule while O_1 and O_2 are not in contact with all three oxygen atoms of any other molecule.

The bond lengths in cyclopentadienyl manganese tricarbonyl are discussed at the end of section IV along with the bond lengths in cyclopentadienyl nickel nitrosyl.

IV. An Electron Diffraction Investigation of Cyclopentadienyl Nickel Nitrosyl

Cyclopentadienyl nickel nitrosyl, C_5H_5NiNO (fig. 14), is a dark red liquid prepared by treating nickelocene with nitric oxide (19). It has a boiling point of 49°C at 27 mm (19) and therefore is suitable for investigation by electron diffraction. A structure investigation of this compound was initiated in the hope that the interatomic distances thus obtained would give additional information about the electronic configuration of cyclopentadienyl metal compounds and their derivatives.

The sample used in this investigation was prepared and supplied by Professor Wilkinson. Diffraction pictures were taken on Kodak 50 plates under the following experimental conditions: 40 kv electrons ($\lambda = 0.06234$ A); camera distance 9.627 cm. The sample bulb was heated to 43°C and exposures of from 2 sec. to 5 min. were made.

The visual data, which extend to $q = \frac{10}{\pi} S = 115$, were analyzed by the standard methods used in this Laboratory (5) to give the radial distribution curve (fig. 15). The fit between the final model (Model A as refined by least squares) and the radial distribution curve is illustrated. On both radial distribution curves* the 1.65 A peak (Ni-N) has an outer shoulder. This feature appears to be the result of errors in the visual interpretations.

The correlation method was employed with the radial distribution curves used as a guide. Curves were calculated for both models with C_{5v}

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* V.S. and A.B.

C_5H_5NiNO

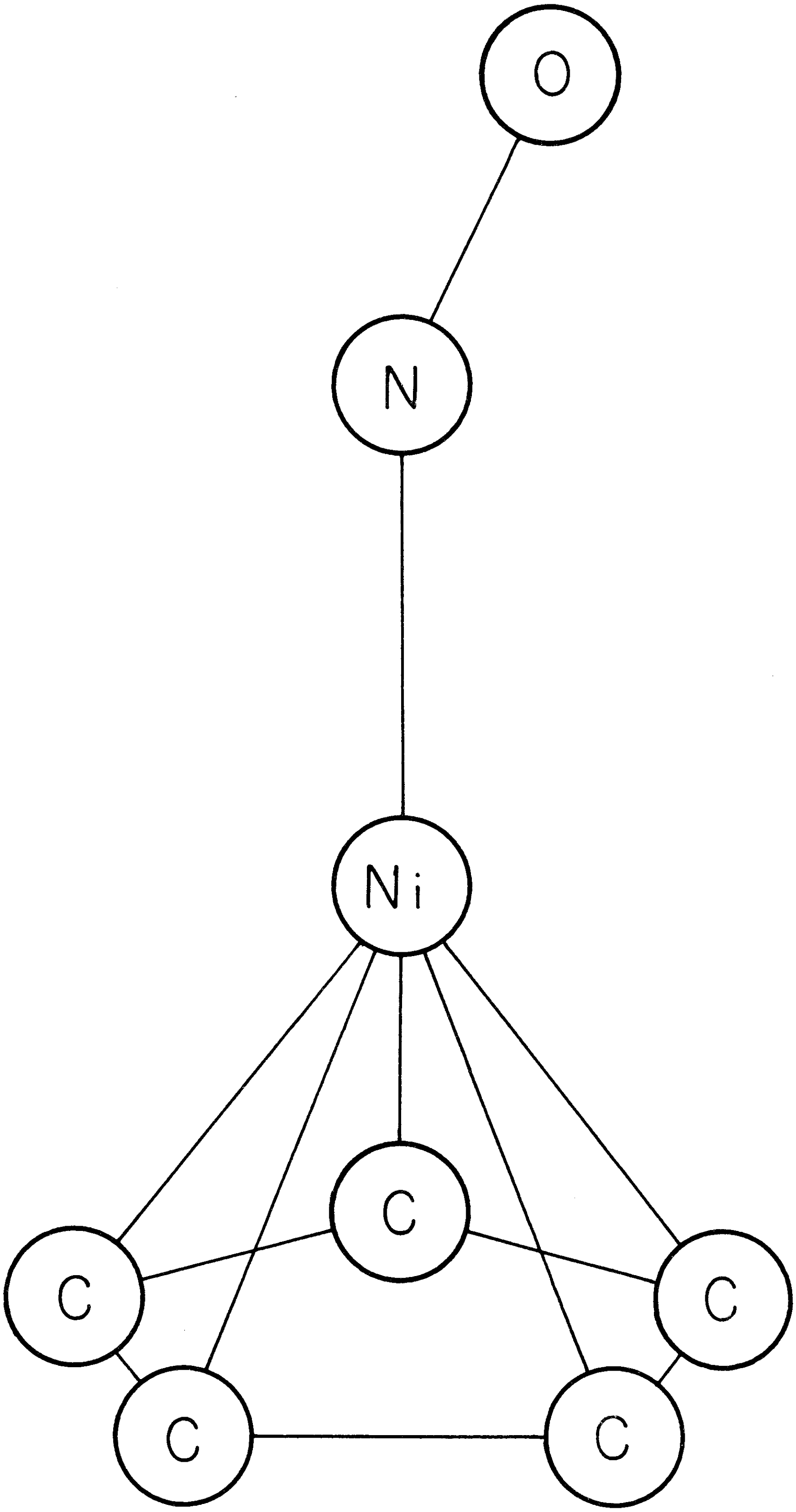

Figure 14

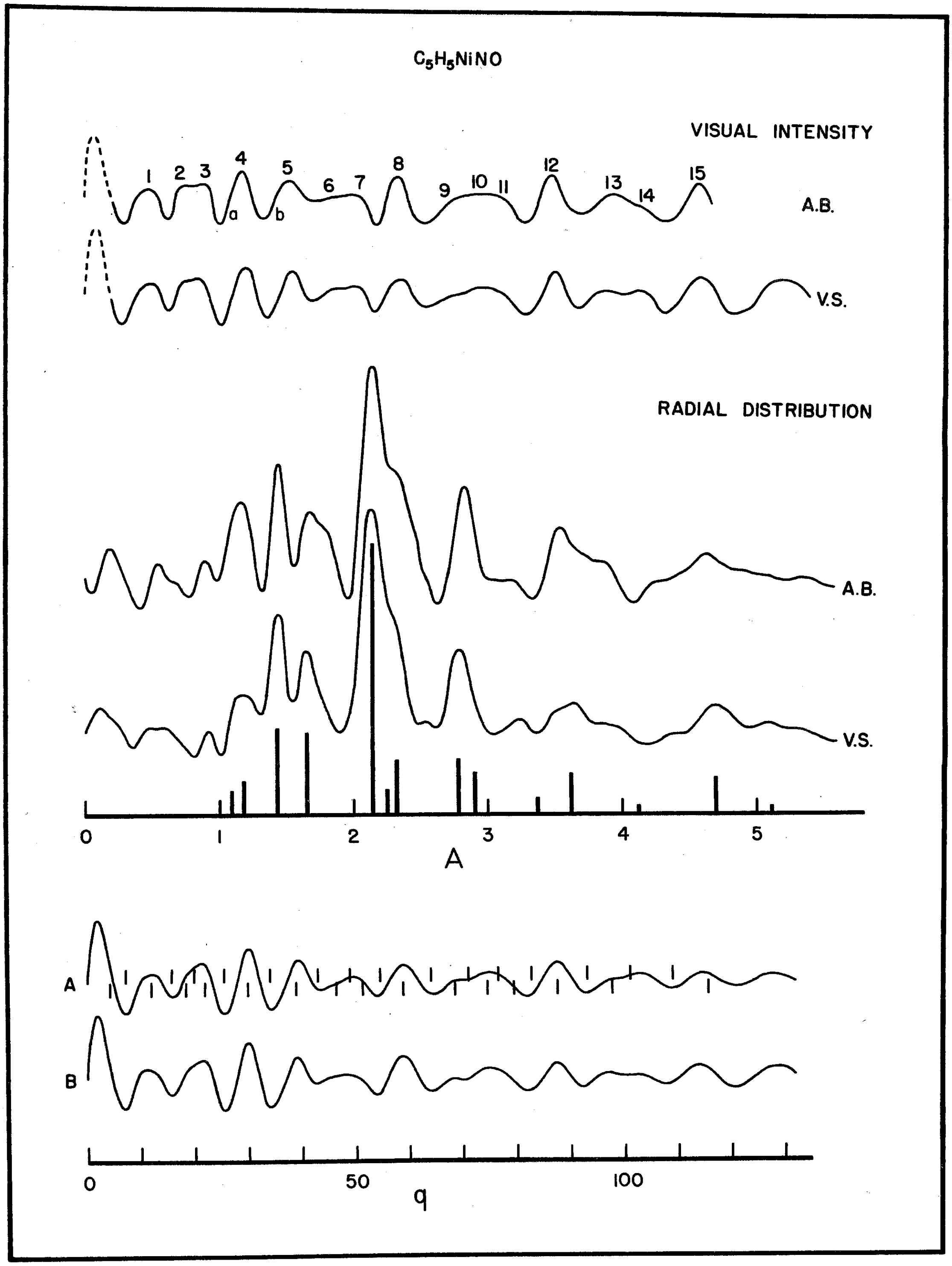
C_5H_5NiNO
VISUAL INTENSITY
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
a
b
A.B.
V.S.
RADIAL DISTRIBUTION
A.B.
V.S.
0
1
2
3
4
5
A
A
B
0
50
100
q

Figure 15

symmetry and models with this symmetry destroyed by moving the oxygen atom off the five-fold axis. The scale parameter was chosen as C-C and the ratio C-H/C-C = 1.09/1.44 was assumed. The hydrogen atoms were assumed to be in the plane of the cyclopentadienyl ring. The effective value 1.25 was used for Z_H. All terms were included except H...H and O...H. Parameters were varied over the following ranges:

$$2.12 \text{ A} \leqslant \text{Ni-C} \leqslant 2.16 \text{ A}$$

$$1.60 \text{ A} \leqslant \text{Ni-N} \leqslant 1.71 \text{ A}$$

$$1.13 \text{ A} \leqslant \text{N-O} \leqslant 1.20 \text{ A}$$

$$2.76 \text{ A} \leqslant \text{Ni-O} \leqslant 2.83 \text{ A}$$

$$0.0015 \leqslant a_{\text{Ni-C}}^{*} \leqslant 0.0025$$

The temperature factors for all other distances were kept constant throughout the investigation and are listed in Table 14.

Of all the models calculated, curve A (fig. 15, Table 14) was judged to have the best fit with the visual curves. This curve is based on the asymmetric model** with $\measuredangle$ O-N-Ni equal to 158°7'. However, curve B (fig. 15, Table 14) based on a model with C_{5v} symmetry cannot be rejected.

Maximum 6 was observed to be a shoulder on the inside of maximum 7 which in itself was observed to be weak. The region around q = 75 was difficult to estimate but was finally judged to be a weak tripled maximum.

---

* $a_{ij} = 1/2(\langle \delta r_{ij}^2 \rangle - \langle \delta r_{C-C}^2 \rangle)$

** No attempt was made to determine the relationship between the oxygen atom and the ring because of the low weight of the O...C term.

Table 14

Distances used in calculating models

	Model A		Model B	
	Dist.	a_{ij}	Dist.	a_{ij}
Ni-C	2.14 A	0.0023	2.14 A	0.0020
C-C	1.44	0	1.44	0
C-H	1.09	0.0015	1.09	0.0015
Ni-N	1.65	0.0018	1.65	0.0018
N-O	1.18	0	1.13	0
Ni-O	2.78	0.0018	2.78	0.0018
C...C	2.33	0.0010	2.33	0.0010
C..H	2.26	0.0031	2.26	0.0031
C...H	3.37	0.0052	3.37	0.0052
Ni...H	2.90	0.0052	2.90	0.0052
N...C	3.62	0.0042	3.62	0.0042
N...H	4.12	0.0064	4.12	0.0064
O...C	4.68 (ave.)	0.0042	4.70	0.0042
O...H	5.10	∞	5.11	∞
$\sphericalangle$ O-N-Ni	$158^{\circ}7'$			

Theoretical curves which have an uncomplicated feature here, or a feature which, if present in the diffraction pattern, could be easily observed to be different from what is drawn in the visual curve, were rejected. Minimum 9 was observed to be broader than minimum 12. Curves A and B represent the observations satisfactorily.

The use of the ordinary correlation method for refining the parameter values and estimating the limits of error did not seem advisable in view of the large number of parameters involved. Instead, the method of least squares was used (24).

The data to be used for the least squares treatment must be taken as the actual visual estimations made from examinations of the plates. These data cannot be read directly from a visual intensity curve since in drawing a visual intensity curve a correlation of the errors in the observations is effectively accomplished. The plates were reexamined (by A.B.) in order to make quantitative comparisons for use in the least squares treatment. In order to minimize correlations among the errors in the observations, an effort was made to estimate three-fold comparisons independent of the associated two-fold comparisons and vice versa. The necessary partial derivatives were calculated using the curves drawn for the correlation procedure. Features other than direct amplitude comparisons (e.g., appearance of a "bump" on the outside of minimum 5, appearance of features at about $q = 75$, etc.) were treated by estimating quantitatively, from the theoretical curves, their deviation from acceptability. Relative weights for individual observations were assigned on the basis of the estimated reliabilities of the observations. These weights were chosen as the reciprocal of the square of the expected error.

The observations used and their relative weights are tabulated in Table 15. The ratios of the averages of the weighted squares of the residuals for the two classes of observations (i.e., positional measurements and amplitude comparisons) for the two models are:

Ratio	Model A	Model B
Amp./Pos.	1.23	1.20

A least squares refinement was made for both models A and B using as parameters C-C, Ni-C, Ni-N, N-O, Ni-O (model A only) and an amplitude scale factor. The calculated shifts and their estimated standard deviations are:

Model A

Parameter	Shift	σ
C-C	-0.007 A	0.0037 A
Ni-C	0.003	0.0044
Ni-N	-0.004	0.0115
Ni-O	0.004	0.0090
N-O	0.000	0.0088

Model B

Parameter	Shift	σ
C-C	-0.004 A	0.0055 A
Ni-C	0.005	0.0039
Ni-N	-0.011	0.0095
N-O	0.024	0.0085

Table 15

Observations

Maxima	Obs.[*]	Weight[**]	Minima	Obs.	Weight
2-1	10	5	4-5	17	9
3-2	15	5	5-6	50	3
4-3	46	6	5-8	16	3
4-5	25	9	8-6	43	3
5-6	88	2	8-9	11	9
5-7	78	2	12-9	18	6
5-8	23	3	12-13	13	6
7-6	8	9			
8-7	33	5			
8-10	32	5			
10-9	18	2			
12-10	50	3			
12-13	50	3			
13-14	18	1			
12-8	19	4			
1,3-2	12	12	5-4,6	26	22
2,4-3	7	8	4-5,2	26	15
1,4-3	29	15	5,8-6	45	3
4-3,5	47	3	8-6,9	28	15
5-4,7	23	15	8,12-9	25	15
4,8-5	13	8	12-9,13	30	3
6,8-7	16	8			
8-7,10	48	2			
8,12-10	55	2			
12-13,10	45	2			

---

[*] An amplitude scale factor was included as a parameter in the least squares treatment.

[**] For model B the two-fold comparisons were included with half the listed weights because of the large value of the sum of the squares of the residuals for this class of observations.

[***] Three-fold comparisons were made by estimating the amount that the middle maximum (minimum) lies above or below a straight line joining the two end maxima (minima). The symbol 1,3-2 means that maximum 2 was observed to lie below the straight line joining maxima 1 and 3 by the observed amount. The symbol 4-3,5 indicates that maximum 4 was observed to be higher than the average of maxima 3 and 5. For minima, e.g., the symbol 5-4,6 indicates that minimum 5 was observed to be deeper than the average of minima 4 and 6.

Table 15 (Cont'd)

Positional Measurements

Max.	Min.	V.S.	A.B.	Ave.	Weight
	1	7.28	7.06	7.17	0
1		11.84	11.94	11.89	0
	2	15.62	15.50	15.56	0
2		18.58	17.93	18.26	0
	3	19.51	20.05	19.78	0
3		20.89	22.81	21.85	0
	4	25.47	25.28	25.38	65
4		29.87	29.45	29.66	78
	5	34.17	33.53	33.85	104
5		39.24	38.21	38.72	104
	6	42.64	42.93	42.78	0
6		46.43	46.01	46.22	0
	7	48.70		48.70	0
7		50.85	51.53	51.19	0
	8	54.29	54.54	54.42	104
8		59.16	58.14	58.65	78
	9	64.17	63.56	63.86	65
9		67.79	68.72	68.26	0
	10	70.87		70.87	0
10		74.31		74.31	0
	11	76.30		76.30	0
11		79.31	79.34	79.32	0
	12	82.74	82.26	82.50	65
12		88.17	86.53	87.35	104
	13	92.66	93.08	92.87	39
13			98.31	98.31	0
	14	100.87		100.87	0
14					
	15	108.60		108.60	13
15		115.95	114.54	115.24	13
a		27.43	27.34	27.38	0
b		36.13	35.87	36.00	0

An additional contribution to the standard deviations due to errors in measuring the electron wave length and the camera distance was estimated to be 0.002 A for r = 1 A and was included in the treatment by assuming $\sigma^2_{(T)} = \sigma^2_{(L.S.)} + (0.002)^2 r^2$. Hamilton estimates (25) that a satisfactory approximation to the usual limit of error is $2\sigma_{(T)}$. The final parameter values and their estimated limits of error are:

Model A

Parameter	Value	$2\sigma_{(T)}$
C-C	1.433 A	0.009 A
Ni-C	2.143	0.012
Ni-N	1.646	0.024
Ni-O	2.784	0.021
N-O	1.180	0.018
∢ Ni-N-O	159°57'	

Model B

Parameter	Value	$2\sigma_{(T)}$
C-C	1.436 A	0.012 A
Ni-C	2.145	0.012
Ni-N	1.639	0.020
N-O	1.154	0.018

The calculated interatomic distances for the refined models are tabulated in Table 16. The correlation matrices are: (Both matrices

Table 16

Final Calculated Distances

	Model A Dist.	Model B Dist.
C-C	1.433 A	1.436 A
C-H	1.09	1.09
C...C	2.319	2.322
C..H	2.253	2.256
C...H	3.373	3.377
Ni-C	2.143	2.145
Ni...H	2.905	2.907
Ni-N	1.646	1.639
N...C	3.619	3.615
N...H	4.117	4.113
Ni...O	2.784	2.793
N-O	1.180	1.154
O...C	4.695 (ave.)	4.717
O...H	5.088	5.109
∢ O-N-Ni	159°57'	180°

are symmetric about the main diagonal.)

Model A

$$\begin{array}{lcccccc}
\text{Amp. S. F.} & 1 & 0.01 & 0.33 & 0.57 & -0.08 & -0.37 \\
\text{C-C} & & 1 & 0.17 & 0.16 & -0.46 & 0.21 \\
\text{Ni-C} & & & 1 & 0.27 & -0.27 & -0.16 \\
\text{Ni-N} & & & & 1 & -0.42 & -0.31 \\
\text{Ni-O} & & & & & 1 & -0.14 \\
\text{N-O} & & & & & & 1
\end{array}$$

Model B

$$\begin{array}{lccccc}
\text{Amp. S. F.} & 1 & 0.65 & 0.06 & 0.71 & -0.20 \\
\text{C-C} & & 1 & -0.02 & 0.15 & -0.55 \\
\text{Ni-C} & & & 1 & 0.12 & -0.25 \\
\text{Ni-N} & & & & 1 & -0.59 \\
\text{N-O} & & & & & 1
\end{array}$$

A preliminary report on an electron diffraction study of nickelocene (16) gives the following parameters for a model with D_5 symmetry: $C-C = 1.43$ A; $Ni-C = 2.20$ A. The shorter (2.143 A) Ni-C bond length in cyclopentadienyl nickel nitrosyl is consistent with the greater stability of this compound.

Table 17 lists the values of the observed metal-carbon (carbonyl) distances and carbon-oxygen distances for several metal carbonyls and related compounds. The single bond radii of the metals (14) and the observed shortening in the metal-carbon bond, i.e., the difference between the sum of the single bond radii of the metal and carbon and the observed metal-carbon bond length, are also tabulated. The carbon-oxygen distance in carbon dioxide is given for comparison. Similarly, in Table 18 are listed corresponding results for metal nitrosyl compounds. The nitrogen-oxygen distance in several inorganic compounds is also listed.

In compounds which have both a carbonyl and nitrosyl group attached to the metal atom, i.e., $Fe(CO)_2(NO)_2$ and $Co(CO)_3(NO)$, the observed difference between the metal-carbon and metal-nitrogen distances is equal to 0.07 A which is exactly equal to the difference in the single bond radii of carbon and nitrogen (14), 0.77 A and 0.70 A. For this reason, it was decided to treat the metal-carbon and metal-nitrogen bond distances together.

Fig. 16 is a graph of the observed shortening of the metal-carbon and the metal-nitrogen distances plotted against the column in the periodic table to which the metal belongs. The upper curve is for compounds containing a cyclopentadienyl group while the lower curve is for compounds which do not contain a cyclopentadienyl group. A comparison of the results for these two classes of compounds indicates that there is an extra shortening of about 0.10 A in the metal-carbon (nitrogen) bond in cyclopentadienyl carbonyl and cyclopentadienyl nitrosyl compounds over the corresponding distance in similar compounds not containing a cyclo-

Table 17

Table of Distances in Metal Carbonyls and Related Compounds

Compound	Metal-carbon distance	Limit of error	C-O distance	Limit of error	Single-bond radius of metal (14)	Shortening of M-C bond[1]	Reference
CO_2			1.15 A	0.02 A			26
$Cr(CO)_6$	1.92 A	0.04 A	1.16	0.05	1.18 A	0.03 A	27
$Mo(CO)_6$	2.06	.04	1.14	.05	1.30	.01	27,28
$W(CO)_6$	2.07	.04	1.13	.05	1.30	.00	27,28
$Fe(CO)_5$	1.84	.03	1.15	.04	1.17	.10	27,28
$Ni(CO)_4$	1.82	.03	1.15	.02	1.15	.10	27,28
$Fe(CO)_4H_2$	1.84[4]	.03	1.15	.05	1.17	.10	27,28
$Fe(CO)_2(NO)_2$	1.84	.02	1.15	.03	1.17	.10	27,28
$Co(CO)_4H$	1.83[4]	.02	1.16	.05	1.16	.10	27,28
$Co(CO)_3(NO)$	1.83	.02	1.14	.03	1.16	.10	27,28
$C_5H_5Mn(CO)_3$	1.77[3]	.03[2]	1.17	.04[2]	1.17	.17[3]	18
$C_5H_5Mo(CO)_3$	1.96[3]	.02[2]	1.17	.02[2]	1.30	.11[3]	29

---

[1] $R(1)$ metal $+ 0.77 - D_{obs.}$

[2] σ, not limit of error

[3] Metal-carbonyl bond

[4] Metal-carbonyl carbon bond is (0.05-0.08 A) shorter

Table 18

Table of Distances in Metal Nitrosyls and Related Compounds

Compound	Metal-Nitrogen distance	Limit of error	N-O distance	Limit of error	Single-bond radius of metal (14)	Shortening of M-N bond[1]	Reference
NO_2			1.19 A	0.004 A			30
N_2O_4			1.18	[2]			30
NO Cl			1.14	0.04			27,28
NO Br			1.15	.04			27,28
$Fe(NO)_2(CO)_2$	1.77 A	0.02 A	1.12	.03	1.17 A	.10 A	27,28
$CO(CO)_3(NO)$	1.76	.02	1.10	.04	1.16	.10	27,28
C_5H_5Ni NO (A)	1.65	.02	1.18	.02	1.15	.20	29
C_5H_5Ni NO (B)	1.64	.02	1.15	.02	1.15	.21	29

---

[1] R(1) metal + 0.70 - $D_{obs.}$

[2] Not given

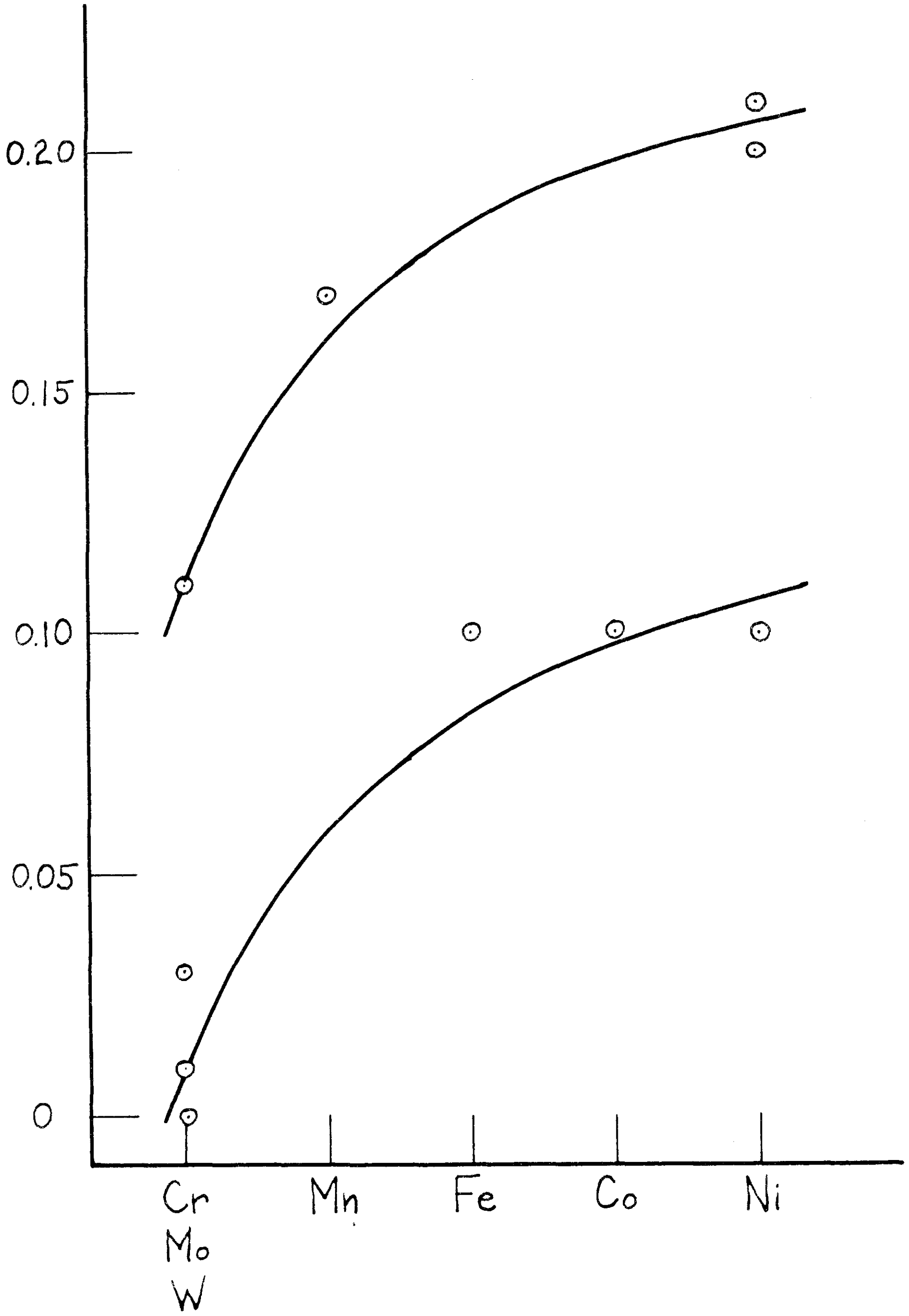

Figure 16

pentadienyl group. The increase in the observed shortening, i.e., increase in the double bond character, going from chromium to nickel, may be explained by the fact that the relative number of d electrons, per bond, available for π-bonding becomes greater as the atomic number increases (31).

The shortening of the metal-carbon (nitrogen) bond is accompanied by an increase in the length of the carbon (nitrogen)-oxygen bond. (Since the results for $Fe(CO)_2(NO)_2$ and $Co(CO)_3(NO)$ are for a linear metal-nitrogen-oxygen bond, the results for C_5H_5NiNO model B may afford a more reasonable comparison than those for model A. In the investigations of the above compounds, the effect of bending of the metal-nitrogen-oxygen bond was not considered.)

Table 19 lists the observed values for the metal-carbon (ring) and carbon-carbon distances in several cyclopentadienyl metal compounds. The metal-carbon (ring) distances in the mixed cyclopentadienyl carbonyl and cyclopentadienyl nitrosyl compounds are considerably lengthened relative to the iron-carbon bond in ferrocene, which may be taken as a standard for metal-cyclopentadienyl bonding. The indication is therefore that the strengthening of the bonds to the carbonyl and nitrosyl groups is accomplished at the expense of weakening the bonding to the cyclopentadienyl ring.

For almost all the metal compounds listed, the central metal atom is surrounded by eighteen electrons if the following electron contributions from the attached groups are assumed: C_5H_5, 5; CO, 2; NO, 3; COH, 3. The only two exceptions are $C_5H_5Mo(CO)_3$ and $C_5H_5NiC_5H_5$

Table 19

A Brief Summary of Results for Cyclopentadienyl Metal Compounds

Compound*	Metal-carbon distance (ring)	C-C distance	Method	Reference
Cy Fe Cy	2.064 A	1.440 A	e.d.	29
Cy Fe Cy	2.03	1.43	e.d.	11
Cy Ni Cy	2.20	1.43	e.d.	16
Cy Ni NO	2.143	1.433	e.d.	29
Cy Fe Cy	2.045	1.403	X-ray	9d
Cy $Mn(CO)_3$	2.146	1.390	X-ray	29
Cy $Mo(CO)_3$	2.345	1.416	X-ray	18

* Cy $\equiv C_5H_5$

which have respectively seventeen and twenty electrons surrounding the metal atom. However, $C_5H_5Mo(CO)_3$ forms a dimer in the crystal and therefore has a stable configuration. Nickelocene is an extremely unstable compound, as suggested by the long (2.20 A) nickel-carbon distance.

APPENDIX

Observed and Calculated Structure Factors for Cyclopentadienyl Manganese Tricarbonyl*

Observed Reflections

$0\ 0\ \ell$

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
2	878	-1067
3	223	-273
4	388	320
5	267	-269
6	385	-316
7	194	201
8	312	356
9	186	-204
10	150	-184
11	77	31
12	81	87

$2\ 0\ \ell$

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
-12	154	-150
-11	65	2
-10	146	127
-9	97	80
-8	267	-192
-7	166	128
-6	522	496
-4	1022	-1358
-3	720	819
-2	829	976
-1	562	-636
0	1059	-1348
1	514	592
2	206	-206
3	210	-191
4	364	-413
5	518	561
6	271	234
7	295	-345
8	89	-102
9	198	231
11	102	-102

$4\ 0\ \ell$

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
-12	170	186
-10	150	-144
-8	420	473
-7	437	-381
-6	610	-758
-5	331	339
-4	578	596
-3	339	-355
-2	121	156
-1	117	-113
0	489	588
1	618	-787
2	52	42
3	506	488
4	150	176
5	271	-294
7	206	219
9	146	-205

$6\ 0\ \ell$

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
-12	243	-288
-11	202	201
-10	218	289
-9	129	-103
-8	308	-288
-7	433	435
-6	121	35
-5	312	-310
-4	235	-300
-3	578	696
-2	295	340
-1	481	-389
0	250	-290
1	400	468
2	198	-284
3	308	-347

---

* All structure factors are multiplied by ten.

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
	6 0 ℓ	
5	250	340
7	129	-182
	8 0 ℓ	
-13	109	140
-12	125	170
-11	247	-238
-9	133	78
-7	380	-408
-5	420	500
-3	481	-591
-1	247	210
0	113	-91
1	319	-393
2	202	338
3	271	366
4	97	-122
5	113	-177
	10 0 ℓ	
-11	162	128
-10	133	-132
-9	166	-151
-7	291	329
-6	102	-112
-5	174	-99
-4	198	230
-3	210	234
-2	227	-268
-1	239	-246
0	177	223
1	125	185
2	121	-227
	12 0 ℓ	
-11	97	-119
-10	109	156
-9	117	108
-7	158	-210
-6	73	108
-5	102	114
-4	142	-205
-2	121	194
0	85	-91
	0 1 ℓ	
2	344	-403
3	190	205
4	174	-140
5	304	-346
6	113	96
7	146	133
9	44	-53
	1 1 ℓ	
-11	102	-131
-10	52	-26
-9	125	90
-8	150	182
-7	465	-453
-6	146	-69
-5	631	617
-4	117	128
-3	388	-359
-2	223	247
-1	809	1068
0	368	-365
1	1055	-1132
2	206	201
3	449	476
4	295	-297
5	339	-252
6	206	167
7	267	207
8	250	-269
10	65	103

2 1 ℓ

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
-10	56	29
-9	48	78
-7	117	-149
-6	77	80
-5	218	-282
-4	89	-85
-3	663	866
-2	356	374
-1	202	199
0	339	351
1	631	632
2	295	-244
4	137	134
5	52	-74
6	65	-38

3 1 ℓ

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
-11	194	192
-9	174	-152
-8	65	-51
-7	541	504
-6	235	-217
-5	610	-579
-4	106	73
-3	372	329
-2	279	-278
-1	772	-769
0	631	616
1	331	311
2	433	-355
3	239	-176
4	312	271
5	170	126
6	223	-211
8	223	294
10	102	-106

4 1 ℓ

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
-11	69	102
-9	106	85
-8	48	-64
-7	263	-335

ℓ	$\lvert F_{obs}\rvert$	F_{calc}

4 1 ℓ

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
-5	154	174
-3	263	305
-2	275	-282
-1	319	-386
1	202	207
2	117	-112
3	158	-135

5 1 ℓ

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
-11	247	-263
-9	194	146
-8	93	-69
-7	380	-403
-6	408	397
-5	460	505
-4	433	-410
-3	271	-248
-2	295	238
-1	372	362
0	360	-323
2	396	377
3	77	78
4	348	-400
6	142	181

6 1 ℓ

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
-9	125	-140
-7	93	-37
-6	210	279
-5	210	250
-4	198	-269
-3	202	-110
-2	85	-73
0	146	-128
1	40	-63

7 1 ℓ

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
-13	52	-106
-12	97	123

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	7 1 ℓ	
-11	194	199
-10	182	-172
-9	154	-130
-8	231	196
-7	214	239
-6	404	-399
-5	106	-89
-4	425	400
-3	33	-17
-2	335	-314
-1	142	-215
0	416	449
1	113	-155
2	356	-343
4	214	257
	8 1 ℓ	
-9	113	23
-8	97	126
-7	109	-52
-6	89	-78
2	73	-49
	9 1 ℓ	
-12	146	-151
-10	194	201
-9	44	8
-8	214	-185
-7	61	-59
-6	295	234
-5	113	-85
-4	323	-362
-3	150	190
-2	331	355
-1	97	-36
0	235	-277
1	121	203
2	125	113
3	113	-120

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	10 1 ℓ	
-10	73	-20
-9	89	-92
-7	97	29
	11 1 ℓ	
-12	117	110
-10	158	-132
-9	97	72
-8	146	203
-6	162	-223
-5	125	145
-4	146	189
-3	146	-225
-2	102	-116
-1	121	94
0	97	111
1	93	-154
	0 2 ℓ	
0	182	157
1	368	-410
2	106	59
3	121	119
4	724	737
5	258	-291
6	412	-357
7	137	137
8	194	121
9	133	-153
10	97	-26
11	85	98
	1 2 ℓ	
-7	81	-86
-6	61	83
-5	117	-84
-4	214	-238

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	1 2 ℓ	
-3	109	-99
-2	339	378
-1	271	269
0	177	-239
1	65	-59
2	368	-411
3	154	178
4	52	32
5	102	80
6	61	75
7	65	-62
10	52	-22
	2 2 ℓ	
-10	133	129
-9	113	121
-8	396	-410
-7	65	-33
-6	469	492
-5	166	197
-4	308	-304
-3	125	-118
-2	177	-158
-1	150	156
0	1019	-1108
1	764	811
2	631	586
3	202	-148
4	412	-392
5	186	141
6	190	96
7	202	-169
9	137	164
	3 2 ℓ	
-8	113	151
-7	69	60
-6	40	-20
-5	166	164
-4	133	125
-3	109	-102
	3 2 ℓ	
-2	526	-619
-1	174	144
0	40	-36
3	113	91
4	93	95
7	73	-95
	4 2 ℓ	
-12	150	195
-11	69	-38
-10	142	-152
-8	291	239
-7	182	-166
-6	250	-215
-5	150	97
-4	506	601
-3	465	-516
-2	506	-435
-1	510	419
0	574	564
1	663	-670
2	125	-48
3	275	228
4	186	211
5	295	-281
6	77	-36
7	194	189
	5 2 ℓ	
-10	93	36
-9	117	-127
-8	102	-63
-7	61	-32
-5	158	-186
-4	48	-33
-3	129	109
-2	69	-77
-1	77	-61
0	174	-198
1	48	52

ℓ	$\|F_{obs}\|$	F_{calc}
	5 2 ℓ	
2	85	-118
3	56	87
4	69	-59
5	150	-167
	6 2 ℓ	
-12	133	-129
-11	129	99
-10	77	17
-9	69	-33
-8	275	-252
-7	331	300
-6	258	321
-5	368	-342
-4	250	-268
-3	465	418
-1	331	-230
0	113	-130
1	529	536
3	291	-246
5	129	128
7	109	-87
	7 2 ℓ	
-9	102	103
-7	97	0
-5	56	-46
-4	102	-108
-3	214	237
-2	106	101
-1	89	106
1	194	204
	8 2 ℓ	
-12	117	108
-11	190	-192
-10	69	-114
-9	174	169
-8	231	285

ℓ	$\|F_{obs}\|$	F_{calc}
	8 2 ℓ	
-7	316	-276
-6	69	-48
-5	254	162
-4	73	-25
-3	348	-368
-1	348	319
1	206	-215
2	77	107
	9 2 ℓ	
-10	52	29
-9	52	-15
-7	81	-84
-5	65	-53
-3	125	60
-1	125	-123
	10 2 ℓ	
-11	227	250
-9	166	-154
-8	69	-72
-7	239	243
-6	102	-73
-5	223	-265
-4	129	107
-3	210	290
-2	77	-87
-1	129	-125
2	117	-128
	11 2 ℓ	
-5	109	163
-3	77	-27
	12 2 ℓ	
-11	150	-150
-7	125	-175

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	12 2 ℓ	
-6	102	142
-5	77	87
-4	125	-135
-2	97	133
0	102	-141
	0 3 ℓ	
2	73	-81
3	380	-350
4	73	-27
5	182	192
6	85	-62
7	73	-46
8	52	-12
9	44	64
	1 3 ℓ	
-11	106	-154
-9	214	205
-8	190	194
-7	360	-343
-5	356	280
-4	52	47
-3	522	-545
-2	170	-191
-1	655	656
0	170	-137
1	420	-352
2	239	217
3	392	347
4	158	-153
5	385	-384
6	275	264
7	299	303
8	214	-243
10	93	-101
	2 3 ℓ	
-9	109	-141
-6	56	26

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	2 3 ℓ	
-5	85	126
-4	263	272
-3	102	58
-2	89	-113
-1	210	-157
0	73	-35
1	206	-221
2	137	128
4	85	-71
5	44	22
6	129	132
7	81	44
	3 3 ℓ	
-11	186	194
-9	223	-172
-7	380	392
-6	158	-130
-5	437	-492
-4	271	300
-3	441	460
-2	170	-122
-1	512	-402
0	477	418
1	537	492
2	514	-558
3	445	-476
4	400	428
5	182	174
6	235	-221
7	77	-88
8	125	122
	4 3 ℓ	
-9	102	111
-7	85	119
-6	56	-66
-5	166	-140
-4	239	-234
-3	239	-308
-2	174	170
-1	190	171

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
	4 3 ℓ	
1	52	1
2	65	50
3	93	119
4	97	79
5	40	-34
6	137	-146
	5 3 ℓ	
-11	133	-110
-10	133	145
-9	166	159
-8	137	-111
-7	267	-283
-6	291	283
-5	177	117
-4	392	-380
-3	190	-166
-2	465	476
-1	400	379
0	789	-818
1	170	-160
2	481	437
3	52	14
4	150	-164
5	73	52
6	150	158
	6 3 ℓ	
-11	65	-30
-10	89	-20
-8	85	65
-7	61	47
-6	73	-102
-5	102	-116
-4	113	122
-3	73	102
-2	52	-19
-1	89	88
0	85	-57

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
	7 3 ℓ	
-11	61	86
-10	154	-161
-9	85	-63
-8	177	117
-7	150	129
-6	348	-320
-5	121	-126
-4	514	528
-2	433	-379
0	327	286
1	73	-104
2	73	-87
3	73	76
4	109	128
5	73	-118
6	102	-130
	8 3 ℓ	
-10	56	38
-9	65	9
-8	113	-108
-7	61	50
-6	102	99
0	102	105
	9 3 ℓ	
-12	113	-104
-10	194	192
-9	69	46
-8	250	-254
-7	61	-58
-6	388	388
-5	65	-43
-4	254	-244
-3	73	101
-2	73	44
-1	109	-47
0	170	-193
1	129	120
2	125	122
3	113	120

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	10 3 ℓ	
-9	109	41
-7	109	-104
-6	73	-88
	11 3 ℓ	
-10	162	-202
-8	146	136
-7	102	-103
-6	129	-116
-5	109	117
-4	109	113
-3	129	-142
-2	102	-104
-1	121	144
0	97	133
1	109	-162
	0 4 ℓ	
0	635	673
1	194	-199
4	372	344
5	113	-121
6	275	-219
7	254	195
8	202	213
9	109	-111
10	93	-86
	1 4 ℓ	
-7	56	-11
-4	56	72
-2	194	266
-1	81	-117
0	142	-155
1	52	60
3	81	87
4	69	20
5	109	-86
6	125	-153
7	89	113

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	2 4 ℓ	
-10	133	139
-9	77	80
-8	243	-231
-7	77	-77
-6	227	185
-5	142	-135
-4	433	-443
-3	243	265
-2	489	483
-1	73	55
0	477	-435
1	372	350
2	239	170
3	243	-224
4	243	-224
5	304	303
6	190	175
7	198	-206
8	109	-101
	3 4 ℓ	
-7	73	103
-6	73	35
-4	97	-68
-3	73	25
-2	56	21
-1	40	-27
0	154	172
1	93	-94
2	113	133
3	214	-228
5	125	101
	4 4 ℓ	
-12	109	116
-10	137	-132
-8	254	277
-7	109	-37
-6	186	-190
-5	275	211
-4	279	281
-3	372	-335

ℓ	$\|F_{obs}\|$	F_{calc}
	4 4 ℓ	
-2	283	-237
-1	287	197
0	335	320
1	489	-428
2	133	-105
3	231	193
4	85	41
5	194	-235
6	81	-26
7	150	167
	5 4 ℓ	
-11	40	-39
-8	65	-56
-6	69	13
-5	48	69
-4	56	68
-3	77	-67
-2	190	212
-1	198	-202
0	113	121
1	93	-39
2	48	-74
3	65	-59
	6 4 ℓ	
-12	109	-118
-11	117	106
-10	109	104
-9	117	-90
-8	206	-207
-7	194	169
-6	113	91
-5	319	-312
-4	158	-176
-3	364	374
-2	142	117
-1	335	-272
0	106	-122
1	323	326
5	154	179
7	93	-123

ℓ	$\|F_{obs}\|$	F_{calc}
	7 4 ℓ	
-10	89	-39
-9	56	42
-6	81	-99
-5	146	162
-4	102	127
-3	146	-170
-2	69	-85
-1	117	88
0	81	33
	8 4 ℓ	
-11	129	-118
-10	61	-2
-9	137	125
-8	89	49
-7	291	-285
-6	81	-15
-5	339	345
-4	106	90
-3	198	-206
-2	109	72
-1	177	151
0	117	-110
1	182	-257
3	129	127
	9 4 ℓ	
-9	77	-71
-8	106	20
-7	109	126
-5	97	-111
	10 4 ℓ	
-11	142	129
-9	129	-113
-8	109	20
-7	186	204
-6	117	-76
-5	166	-192
-4	81	42

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	10 4 ℓ	
-3	117	82
-2	117	-144
-1	137	-92
0	129	150
1	102	132
2	56	-119
	0 5 ℓ	
3	61	-63
5	93	114
6	56	-38
	1 5 ℓ	
-4	89	-78
-3	335	-325
-1	372	280
0	81	-85
1	356	-343
2	258	248
3	283	305
4	146	-137
	2 5 ℓ	
-9	44	-52
-8	73	25
-5	73	-71
2	93	116
4	97	-98
5	97	-97
	3 5 ℓ	
-9	137	-159
-7	210	187
-5	162	-86

ℓ	$\lvert F_{obs} \rvert$	F_{calc}
	3 5 ℓ	
-4	186	180
-3	304	274
-2	133	-124
-1	388	-354
0	254	184
1	137	90
2	113	-96
3	44	48
4	106	80
6	150	-187
	4 5 ℓ	
-9	48	41
-6	65	-35
-2	142	130
0	109	109
1	77	83
2	73	-84
4	69	20
	5 5 ℓ	
-11	73	-121
-9	166	156
-8	89	4
-7	243	-220
-6	73	100
-5	210	212
-4	254	-231
-3	194	-186
-2	146	74
-1	158	94
0	125	-70
2	166	103
	6 5 ℓ	
-8	73	51
-7	56	41
-4	52	54
-2	146	-160
-1	61	-20

ℓ	$\|F_{obs}\|$	F_{calc}
	7 5 ℓ	
-11	73	71
-10	125	-125
-9	106	-111
-8	170	147
-7	154	158
-6	227	-201
-5	106	-76
-4	166	116
-2	166	-90
	8 5 ℓ	
-8	73	-83
-7	65	-20
	9 5 ℓ	
-10	97	98
-8	133	-62
-6	206	144
	0 6 ℓ	
0	312	327
1	129	-138
2	291	-270
3	117	98
4	223	235
6	150	-139
	1 6 ℓ	
-6	97	137
-4	93	-87
-2	106	56
2	162	-173
3	97	93
7	56	-27

ℓ	$\|F_{obs}\|$	F_{calc}
	2 6 ℓ	
-8	117	-104
-7	61	-22
-6	190	188
-5	73	-34
-4	250	-302
-3	137	82
-2	299	283
0	243	-198
1	166	164
2	150	106
5	109	110
6	97	84
7	81	-107
	3 6 ℓ	
-7	48	-48
-5	93	16
-4	93	66
-2	142	-158
-1	206	191
0	77	-92
	4 6 ℓ	
-8	166	201
-7	97	-39
-6	202	-215
-5	137	122
-4	186	147
-3	166	-139
-2	162	-108
-1	125	90
0	142	137
1	206	-171
3	162	130
4	48	-61
5	129	-138

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
	5 6 ℓ	
-7	106	87
-6	73	86
-5	93	-101
-3	113	86
-1	97	-92
0	81	-66
3	117	147
	6 6 ℓ	
-9	97	-117
-8	166	-154
-7	121	112
-6	117	117
-5	137	-85
-3	170	121
-1	263	-201
1	223	219
	7 6 ℓ	
-7	52	-45
-1	73	83
	8 6 ℓ	
-9	102	82
-7	142	-97
-5	166	129
-3	170	-146
	9 6 ℓ	
-6	40	9
	10 6 ℓ	
-7	106	94

ℓ	$\lvert F_{obs}\rvert$	F_{calc}
	0 7 ℓ	
1	146	141
2	65	31
5	65	-22
	1 7 ℓ	
-7	93	-95
-5	166	153
-3	198	-194
-1	250	225
1	186	-148
3	162	110
	2 7 ℓ	
-5	77	-102
-3	102	106
-2	89	-87
-1	113	-80
	3 7 ℓ	
-7	142	150
-5	186	-203
-4	56	71
-3	190	159
-1	198	-153
0	121	109
2	158	-160
3	109	-112
4	137	139
	4 7 ℓ	
-5	102	94
-3	48	-32
0	52	-33
2	97	-37

l	$\lvert F_{obs} \rvert$	F_{calc}
	5 7 l	
-7	117	-129
-6	97	83
-5	93	73
-4	150	-106
-2	186	182
-1	121	92
0	218	-219
2	142	150
	6 7 l	
-4	73	-13
-2	65	-34
	0 8 l	
2	73	-55
4	65	88

l	$\lvert F_{obs} \rvert$	F_{calc}
	1 8 l	
0	52	64
	2 8 l	
-2	73	70
0	113	-153
2	102	94
	4 8 l	
-3	81	-85
-2	133	-119
0	93	103
1	89	-88
	6 8 l	
-3	106	107
-1	77	-78

Unobserved Reflections

Structure factors were calculated for 180 unobserved reflections. Of these only 15 had calculated structure factors larger than the minimum observable values.

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Propositions

1. The formula used by Pauling and Wilson for manipulating Hermite polynomials (1) is a special case of the more general formula

$$\frac{\partial^n}{\partial\alpha^n}F(\alpha,\beta)\Big]_{\alpha=0} = \frac{\partial^n}{\partial(\alpha+A\beta)^n}F(\alpha,\beta)\Big]_{\alpha=0} = \frac{1}{A^n}\frac{\partial^n}{\partial\beta^n}F(0,\beta)$$

A sufficient condition for the validity of this formula is

$$F(\alpha,\beta) = G(\alpha+A\beta) + H(\beta) \quad \text{where} \quad \frac{d^n}{d\beta^n}H(\beta) = 0 \; .$$

2. The McCabe-Thiele method for the calculation of the number of theoretical stages in a distillation process (2) is based on the assumption of no heat transfer from the column. I propose an extension of this method which eliminates the necessity of this assumption, enabling more accurate calculations for cases in which the operating line passes close to the equilibrium curve or cases where the assumption of no heat loss is invalid, e.g. small laboratory installations.

3. I propose a proof of the fact that the determinant of the matrix of coefficients of a set of normal equations is always positive. This may be considered as a generalized Schwarz' inequality since this result reduces to Schwarz' inequality for the case of a two by two matrix.

4. The beam stops used with the layer line screens on the Supper Weissenberg camers in these laboratories are of such large size as to screen several low angle reflections. I propose that smaller beam

stops be made to replace those presently in use.

5. Birmingham and Wilkinson postulate a structure for the tricyclopentadienides of the rare earth elements (3). Their structure is unreasonable because of the large metal-carbon distance which it necessitates. Another structure which eliminates this objection is proposed.

6. I propose a set of experimental conditions which may be useful in determining the nature of the effect of radioactivity on radiocolloid formation, i.e., whether the radiation is necessary for the formation of the radiocolloid or is merely an analytical tool.

7. I propose that, as an aid to visual interpretations of electron diffraction plates, especially by inexperienced observers, the possibility of using positive prints from the negatives as well as the negatives themselves be investigated.

8. A few time saving suggestions for use with Swift's scheme for elemental analysis are proposed.

9a. Cotton, et al. postulate that the structure of $C_5H_5W(CO)_6WC_5H_5$ is a "double decker sandwich" (4), with approximate symmetry mmm. I propose that the structure of this compound should be analogous to that reported for $C_5H_5Mo(CO)_3$ (5).

b. The crystal structure of chromium dibenzene should provide an interesting test of the effect of "sandwich bonding" on the C-C distance in the ring.

10. Sim has calculated the fraction of all the structure factors whose signs are determined by a heavy atom as a function of the relative scattering powers of the heavy atom and of the rest of the molecule (6). Since, in actual practice, only those reflections are used for which the

heavy atom contribution is larger than some arbitrary value a more useful calculation would be the fraction of structure factors whose signs are determined by the heavy atom expressed also as a function of the minimum heavy atom contribution used.

11. Some suggestions for the teaching of Chem. 1 are proposed.

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