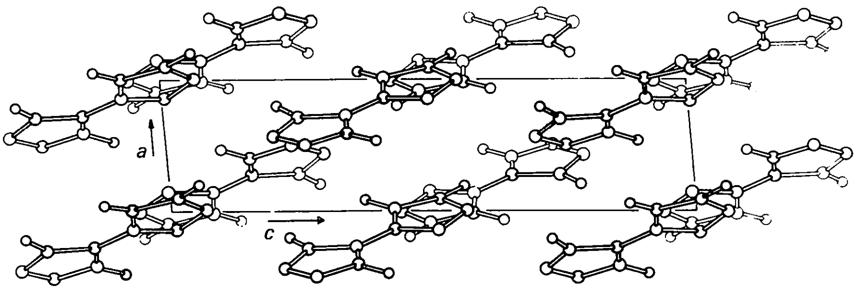

Fig. 5. Projection of the structure along the *b* axis.

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# The Molecular Structure of $Fe(CO)_5$ in the Gas Phase

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New electron diffraction intensity data have been collected for gaseous iron pentacarbonyl, $Fe(CO)_5$. Full-matrix least-squares refinement confirms the trigonal bipyramid molecular structure found in earlier studies. The structural parameters found are: C–O (mean) 1·145 ± 0·003 Å, Fe–C (equatorial) 1·833 ± 0·004 Å, Fe–C (axial) 1·806 ± 0·005 Å, Fe–C (mean) 1·822 ± 0·003 Å. The effects of different weighting schemes, different magnitudes of shrinkage corrections and the use of assumed vibrational amplitudes have been investigated in detail. The results are compared with a parallel study by Almenningen, Haaland & Wahl.

## Introduction

The crystal structure of iron pentacarbonyl, $Fe(CO)_5$, has been investigated by A. W. Hanson (1962), and further refined in an alternative space group by Donohue & Caron (1964). These studies showed that the molecular structure is, within experimental error, a trigonal bipyramid, with the carbon atoms of the carbonyl groups bonded to the iron atom. No significant difference between the axial and equatorial Fe–C bond lengths was found. Davis & Hanson (1965, 1967) have studied iron pentacarbonyl in the gas phase by electron diffraction and concluded that the equatorial Fe–C bond length is longer than the axial Fe–C bond length by 0·049 ± 0·020 Å. This work has been the subject of comment by Donohue & Caron (1966, 1967), who point out that the use of assumed vibrational amplitudes may have prejudiced the refinements of Davis & Hanson. They further question whether the electron diffraction experiment is capable of providing a reliable estimate of this small difference in bond lengths. We have now collected new electron diffraction data for $Fe(CO)_5$. Because determination of the Fe–C bond length difference is certainly difficult with present experimental techniques we have considered in detail the effects of different weighting schemes and different refinement methods on this parameter. After this work was substantially complete, we received the results of a further study carried out at the University of Oslo (Almenningen, Haaland & Wahl, 1968, hereafter referred to as AHW). A comparison between the two sets of results is of interest in establishing the reproducibility of independent gas-phase diffraction studies between different laboratories.

## Experimental

A small, highly pure sample of $Fe(CO)_5$ was donated to us by Dr B. J. Aylett. It was fractionally distilled *in vacuo* before use. Examination by infrared spectroscopy and mass spectrometry failed to reveal the presence of any impurities.

Photographs were taken on Ilford N.60 plates in the Balzers KD.G2 gas diffraction apparatus at the University of Manchester Institute of Science and Technology, using 46 kV electrons, and the photographic intensities were transferred to punched paper tape using an automated Joyce–Loebl microdensitometer (Beagley, Clark & Hewitt, 1968). The electron wavelength used was $0{\cdot}05580_3$ Å with an estimated uncertainty of $0{\cdot}00003_0$ Å. The wavelengths calculated by direct measurement of the voltage and by observation of the T1C1 powder diffraction pattern agreed within this uncertainty. Nozzle-to-plate distances of 100 cm, 50 cm and 25 cm were employed, corresponding to $s$ ranges of approximately 1 to 7, 2 to 14 and 8 to 30 $Å^{-1}$ respectively.

Data reduction and all subsequent calculations were performed using the Cambridge University Titan computer. For each camera distance, centring of individual traces, averaging of all traces and interpolation in even intervals in $s$, and corrections for emulsion response, sector profile and plate planarity were performed by a new program written by two of us (A.G.R. and G.M.S.). Six or more diameters, *i.e.* at least twelve radial traces, were incorporated in the averaged intensities for each camera distance. The $s$ intervals used were $0{\cdot}025$ $Å^{-1}$ for 100 cm plates, $0{\cdot}050$ $Å^{-1}$ for 50 cm plates and $0{\cdot}100$ $Å^{-1}$ for 25 cm plates. From the 'uphill curve', $[s^4I_T(s)]$ our procedure has already been described (Beagley, Robiette & Sheldrick, 1968*a*). Each set of data is scaled to the calculated coherent atomic scattering, after which the data are inspected, and final adjustments to the background and selection of weight functions are performed. Scattering amplitudes and phases were taken from the calculations of Cox & Bonham (1967), interpolated for 46 kV electrons.

## Least-squares refinement

A description of our full-matrix least-squares program has been reported elsewhere (Beagley, Robiette & Sheldrick, 1968*a*). The quantity minimized in the refinement is $\mathbf{U'wU/I'wI}$, where $\mathbf{w}$ is the off-diagonal weight matrix described below, $\mathbf{I}$ the vector of observed intensities $I^{\rm obs}$ and $\mathbf{U}$ the vector $(I^{\rm obs}-I^{\rm calc})$. The expression employed to calculate the theoretical molecular intensity is

$$I^{\rm calc}=k_t \sum_{i\neq j}\sum |f_i|\,|f_j| \cos(\eta_i-\eta_j) \times \sin[s(r_{ij}-\kappa_{ij}s^2)] \exp(-u_{ij}^2s^2/2)/r_{ij}s\,,$$

with a separate scale factor $k_t$ for each camera distance $t$. The $r_{ij}$ are here $r_g(1)$ (Bartell, 1955). Anharmonicities $\kappa_{ij}$ were derived from the relation $\kappa_{ij}=au_{ij}^4/6$. The asymmetry parameter $a$ was fixed but the dependence on $u_{ij}$ explicitly included. $a$ was set equal to $1{\cdot}5$ $Å^{-1}$ for C–O bonds, 2 $Å^{-1}$ for Fe–C bonds and zero for non-bonded distances. Refinement was continued until all shifts were less than one tenth of a standard deviation, except where otherwise mentioned. At this stage most of the shifts were less than $10^{-4}$ Å.

## Weighting schemes

The problem of weighting electron diffraction data in least-squares refinement has no obvious solution. There is general agreement that the data close to the centre of the plate and data at the outer edge of the plate should be weighted down; the former because of uncertainties in the sector profile and in calculated scattering factors at low scattering angles, and the latter because of extraneous scattering from the walls of the chamber and from other parts of the apparatus. Empirical adjustments to the background are also likely to be uncertain at both extremes of each data set. We use (Beagley, Robiette & Sheldrick, 1968*a*) a trapezoidal function, choosing for each camera distance $t$ two points $s_1$ and $s_2$. The diagonal weight matrix elements are then

$$\begin{aligned} w_{kk}&=W_t(s_k-s_{\min})/(s_1-s_{\min}) && s_{\min}\le s_k\le s_1\,;\\ w_{kk}&=W_t && s_1\le s_k\le s_2\,;\\ w_{kk}&=W_t(s_{\max}-s_k)/(s_{\max}-s_2) && s_2\le s_k\le s_{\max}\,. \end{aligned}$$

The off-diagonal matrix elements are given by

$$\begin{aligned} w_{kl}&=0\,, && l\neq k\pm1\\ w_{kl}&=-0{\cdot}5(w_{kk}+w_{ll})\,(p/h)_t\,, && l=k\pm1 \end{aligned}$$

where $(p/h)_t$ is found for each camera distance $t$ by the method of Murata & Morino (1966) [see also Beagley, Robiette & Sheldrick (1968*b*)]. The problem in our treatment arises in choosing the $W_t$, that is the relative total weights to be assigned to batches of data obtained at different camera distances.

Parameters which are well determined, *i.e.* interatomic distances and amplitudes which correspond to well resolved peaks in the radial distribution curve, are not usually sensitive to the weighting scheme. In the present case, however, the difference between equatorial and axial Fe–C bond lengths could well be affected by the choice of weights and we have therefore carried out refinements under weighting schemes which differ widely.

We have employed four different weighting schemes. In the first (I) $W_1(100\text{ cm}) = W_2(50\text{ cm}) = W_3(25\text{ cm}) = 1$. This means that each individual data point is equally weighted (except for down-weighting at the inner and outer parts of a data set). In the second (II) $W_1 = 0{\cdot}25$ $W_2 = 0{\cdot}50$, $W_3 = 1{\cdot}00$. This corresponds to even weighting of a single $s$ unit at each camera distance, since there are twice as many data points per $s$ unit at 100 cm ($\Delta s = 0{\cdot}025$ Å$^{-1}$) as at 50 cm ($\Delta s = 0{\cdot}05$ Å$^{-1}$) and four times as many as at 25 cm ($\Delta s = 0{\cdot}10$ Å$^{-1}$). In the third and fourth weighting schemes (III and IV) the $W_t$ are allowed to vary from cycle to cycle in a manner determined by an analysis of variance.

This analysis provides $(\mathbf{U}'\mathbf{w}\mathbf{U})_t$ and $(\mathbf{U}'\mathbf{w}\mathbf{U}/\mathbf{I}'\mathbf{w}\mathbf{I})_t$ for each camera distance separately. The two weighting schemes dependent on this analysis either (III) aim to make $W_t(\mathbf{U}'\mathbf{w}\mathbf{U}/\mathbf{I}'\mathbf{w}\mathbf{I})_t$ the same for all camera distances, *i.e.* $W_t$ for the next cycle is taken inversely proportional to $(\mathbf{U}'\mathbf{w}\mathbf{U}/\mathbf{I}'\mathbf{w}\mathbf{I})_t$; or (IV) aim to make $(\mathbf{U}'\mathbf{w}\mathbf{U}/N)_t$ the same for all camera distances. $N_t$ here is the 'effective' number of data points for camera $t$, *i.e.* $N_t = (\sum_k w_{kk})_t / W_t$.

### *Molecular model*

The molecular point group $\bar{6}2m$ ($D_{3h}$) was assumed, with a trigonal bipyramidal arrangement of carbonyl groups about the iron atom. The three equatorial C–O groups are numbered C(1)–O(1), C(1′)–O(1′), C(1″)–O(1″), and the two axial groups C(2)–O(2), C(2′)–O(2′). All bonded (C–O) distances were assumed equal. With this restriction the geometrical parameters can be taken as C–O(mean), Fe–C(mean) and [Fe–C(1)]–[Fe–C(2)] = $\Delta$. This enables the estimated standard deviation in $\Delta$ to be conveniently obtained. The bond lengths Fe–C(1), Fe–C(2) and the twelve different non-bonded interatomic distances were calculated from these three parameters in terms of a rigid molecule: the calculated shrinkage effects of Brunvoll (1967) were then subtracted and the resulting values taken to be the $r_g(1)$ required in the theoretical intensity expression. Ideally the rigid-body calculations should be carried out in terms of $r_g(0)$, as AHW have pointed out. We were prompted by their work to carry out a refinement in which bonded distances were first converted to $r_g(0)$ by the addition of $u_{ij}^2/r_{ij}$. The non-bonded distances were then calculated as $r_g(0)$, and converted back to $r_g(1)$ by subtraction of shrinkage and $u_{ij}^2/r_{ij}$. AHW found that the effect on the final parameters was very small but that their fit became worse; we found small changes in the parameters, although our fit was slightly improved. As amplitudes are seriously affected by systematic errors in the intensity measurements, we believe that the use of $r_g(1)$ values in the geometrical computations is in general to be preferred.

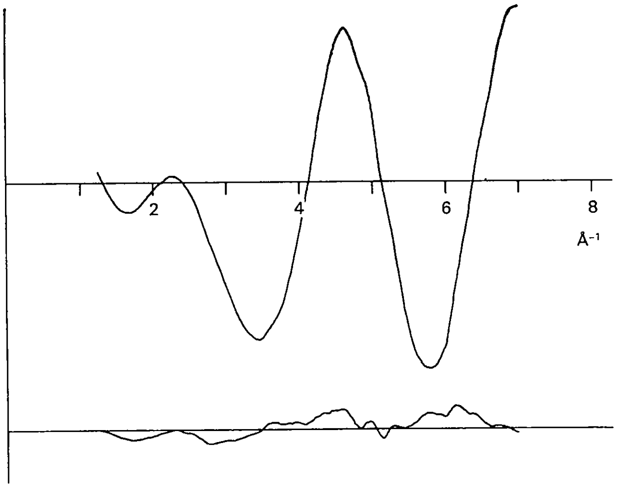

Fig. 1. Observed and weighted difference intensities, camera distance 100 cm.

If $\Delta$ is small, three pairs of distances should give rise to unresolved peaks in the radial distribution $P(r)/r$, with the consequence that the amplitudes involved cannot be independently refined. Thus we have applied the following three constraints:

(*a*) With Fe–C(1) = $r_1$, Fe–C(2) = $r_2$,

$$u_1/u_2 = [(r_1 - d)/(r_2 - d)]^{3/4} = \alpha\,.$$

This constraint is derived from Badger's rule (Bartell & Carroll, 1965; Hansen & Bartell, 1965) and $d$ is a Badger's rule constant set equal to 0·985 Å.

(*b*) $u[\text{Fe–O(1)}] = \alpha\,.\,u[\text{Fe–O(2)}]$

with the same value of $\alpha$. The calculated values of Brunvoll (1967) show that such a ratio is reasonable.

(*c*) $u[\text{C(1)–O(2)}] = u[\text{C(2)–O(1)}]\,.$

While there are in principle fifteen independent amplitudes of vibration, these constraints restrict the refinable amplitude parameters to twelve.

## Results

The separate molecular intensity curves for the 100 cm, 50 cm, and 25 cm camera distances are shown in Figs. 1, 2 and 3. (The uphill curves from which these intensities were derived are available from the authors on request.) The weighted difference intensities plotted below each curve are $w_{kk}^{1/2}(I_k^{\text{obs}} - I_k^{\text{calc}})$.

After every refinement a composite intensity curve was constructed from the three weighted experimental curves, each divided by its least-squares scale factor $k_t$, with the addition of theoretical intensity data to extend the lower $s$ limit to zero (Beagley, Robiette & Sheldrick, 1968*a*). Radial distribution curves $P(r)/r$ were obtained from the composite intensity data by multiplication by $s\,.\exp(-0{\cdot}0025s^2)/|f_o|\,|f_c|$ followed by Fourier inversion. The $P(r)/r$ difference plots contained no prominent features. An example is given in Fig. 4. Fig. 4 and the difference plots in Figs. 1 to 3 result from refinements under weighting scheme I.

### *Weighting scheme* I

Most of the refinements were carried out under weighting scheme I. All twelve amplitude parameters could be refined simultaneously with the three scale factors and the three geometrical parameters. The bonded distances and their amplitudes are given in Table 1, column (*a*). Non-bonded distances and their amplitudes are given in Table 3, cols. (*a*) and (*b*). All uncertainties quoted in these tables are standard deviations estimated in the least-squares analysis. Included in Table 1 are the 'generalized' and 'diagonal' $R$ values defined as

$$R_G=(\mathbf{U'wU}/\mathbf{I'wI})^{1/2},\ R_D=(\sum_k w_{kk}U_k^2/\sum_k w_{kk}I_k^2)^{1/2}\,.$$

Several refinements were carried out for fixed values of $\Delta$ in the range $-0{\cdot}05$ to $0{\cdot}10$ Å. A plot of $R_G$ against $\Delta$ shows a well defined and symmetrical minimum at $\Delta=0{\cdot}028$ Å. From the $R$ index ratio distributions (Hamilton, 1965) the 99·5% confidence interval $0{\cdot}013\le\Delta\le0{\cdot}042$ Å can be established, showing that the marginal standard deviation estimated for $\Delta$ in the general refinement ($0{\cdot}004_6$ Å) is realistic.

Table 1 contains the results of some refinements carried out using weighting scheme I under slightly different conditions. These are: column (*b*), the Badger's rule constraint was replaced by the conditions $u$[Fe–C(1)] = $u$[Fe–C(2)] and $u$[Fe–O(1)] = $u$[Fe–O(2)]; column (*c*), bonded amplitudes were fixed at the values of Brunvoll (1967) and non-bonded amplitudes refined; column (*d*), bonded amplitudes were refined and non-bonded amplitudes fixed at Brunvoll's (1967) values; column (*f*), all amplitudes were refined but no shrinkage corrections were applied.

After these refinements were substantially completed we received a communication on the refinements carried out in Oslo by AHW. These results were similar to ours but with a somewhat smaller value of $\Delta$, $0{\cdot}012\pm0{\cdot}006$ Å. A refinement was therefore carried out on our data with the non-bonded amplitudes fixed at AHW's values: this led to a value of $\Delta=0{\cdot}013_5\pm0{\cdot}004_7$ Å [Table 1, col. (*e*)]. When the non-bonded amplitudes were allowed to refine, however, the structure slowly converged to that given in Table 1, col. (*a*). At this stage the $r_g(0)$ calculation referred to under the *Molecular model* heading above was performed. The results are in Table 1, col. (*h*).

The molecular parameters obtained for a model refined as in Table 1, col. (*a*) but without shrinkage corrections are given in Table 1, col. (*f*). In this refinement one non-bonded amplitude had to be fixed ($u$[C(2)···C(2′)] = 0·2986 Å). The $R$ values are much worse than those in Table 1, col. (*a*). $\Delta$ becomes $0{\cdot}032_9\pm0{\cdot}004_7$ Å. It is clear that when the amplitudes are all allowed to refine freely only one factor, the application of shrinkage corrections, affects $\Delta$ appreciably. This suggested the possibility of applying shrinkage corrections greater than the calculated values, especially as the diagonal force field used by Brunvoll (1967) is inevitably approximate. The relative magnitudes of the calculated shrinkages for each non-bonded distance were maintained, but they were multiplied by a numerical factor which was allowed to vary in the refinement. This refinement [Table 1, col. (*g*)] converged satisfactorily, but the final value of the shrinkage factor, $2{\cdot}4_8\pm0{\cdot}2_4$, is probably too high to be physically realistic. The corresponding value of $\Delta$, $0{\cdot}015\pm0{\cdot}005$ Å,

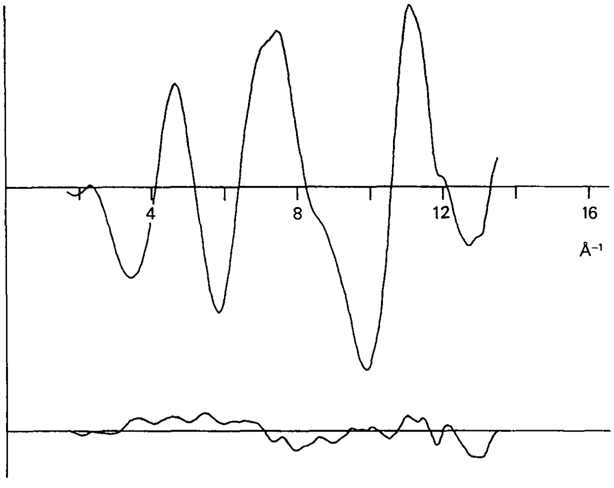

Fig. 2. Observed and weighted difference intensities, camera distance 50 cm.

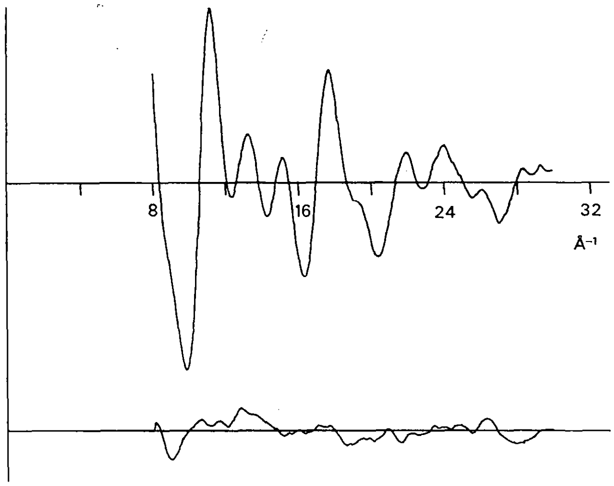

Fig. 3. Observed and weighted difference intensities, camera distance 25 cm.

does show the decrease expected from a consideration of the results in Table 1, cols. (*a*) and (*f*).

### *Weighting scheme* II

Under weighting scheme II the refinement converged to the values given in Table 2, col. (*a*). Table 3 compares the non-bonded amplitudes of weighting schemes I, II, III and IV with those of AHW and Brunvoll (1967). Under all weighting schemes except I the three non-bonded amplitudes which are least well-defined – $u$[C(1)···C(1′)], $u$[C(2)···C(2′)] and $u$[O(1)···O(2)] – did not converge very satisfactorily. Even when all other parameters had converged these three amplitudes continued to oscillate with shifts of the order of a standard deviation. The constraint of these parameters at the values of Table 3, col. (*b*) in no case resulted in a rise in the generalized $R$ index significant at the 1% confidence level (Hamilton, 1965). The value of $\Delta$ using weighting scheme II is 0·022 ± 0·005 Å.

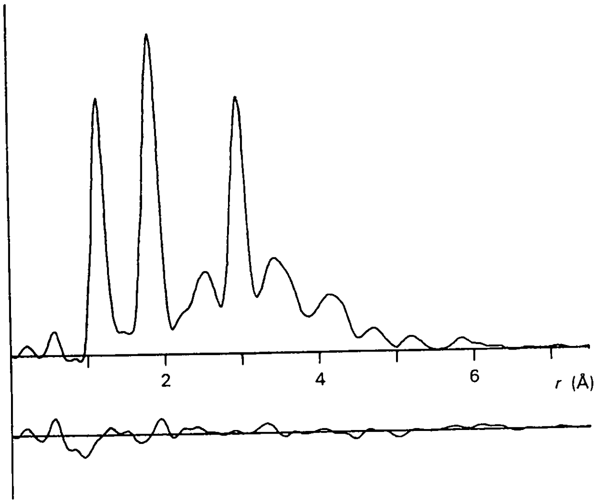

Fig. 4. Observed and difference radial distribution functions $P(r)/r$: artificial temperature factor exp $(-0{\cdot}0025\,s^2)$.

### *Weighting schemes* III *and* IV

The analysis of variance of our data is given in Table 5. The $R_G$ are very similar for the 100 cm data and the 50 cm data, and both are higher than $R_G$ for the 25 cm data. Under scheme III with the $W_t$ scaled so that $W_3(25\text{ cm}) = 1$, $W_1$ and $W_2$ received values in the range 0·6 to 0·7, varying slightly each cycle as the structure altered. The final parameter values, given in Table 2, col. (*b*), are reasonable: $\Delta$ refined to 0·027 ± 0·005 Å.

The criterion that the quantity $(\mathbf{U'wU}/N)$ be made equal for all camera distances resulted in weight factors of 5·3 for the 100 cm data and 0·4 for the 50 cm data relative to a weight factor of 1·0 for the 25 cm data. Although, again, the structure [Table 2, col. (*c*)] is reasonable, these weights are probably too strongly affected by the approximate off-diagonal parameters in the weight matrix to be realistic. The use of $(\mathbf{U'wU/I'wI})_t$ as a criterion of weighting is preferable, since the effect of the weight matrix substantially cancels. It is clear from Table 4, however, that the effect of the off-diagonal parameters in $(\mathbf{U'wU/I'wI})$ is not negligible, since, while $R_G$ is of the same order of magnitude for all camera distances (as is $R_D$), the trends in $R_G$ are opposed to those in $R_D$. $\Delta$ refined to 0·028

Table 1. *Refinements carried out under weighting scheme* I

(*a*) All parameters refined. Badger's rule constraints on $u_{ij}$.
(*b*) As (*a*), but $u$(Fe–C) and $u$(Fe–O) pairs equal.
(*c*) Bonded $u_{ij}$ fixed (spectroscopic values), non-bonded $u_{ij}$ refined.
(*d*) Bonded $u_{ij}$ refined, non-bonded $u_{ij}$ fixed (spectroscopic values).
(*e*) Bonded $u_{ij}$ refined, non-bonded $u_{ij}$ fixed (AHW values).
(*f*) No shrinkage corrections applied.
(*g*) Shrinkage factor refined; all shrinkages multiplied by 2·48 ± 0·24.
(*h*) Geometry calculated on the basis of $r_g(0)$.

The estimated standard deviations in parentheses in column (*a*) apply to all refinements in this Table.

| | *a* | *b* | *c* | *d* | *e* | *f* | *g* | *h* |
|---|---|---|---|---|---|---|---|---|
| Geometrical parameters (Å) | | | | | | | | |
| C–O (mean) | $1{\cdot}145_2$ $(0{\cdot}001_9)$ | $1{\cdot}145_1$ | $1{\cdot}144_9$ | $1{\cdot}143_7$ | $1{\cdot}145_2$ | $1{\cdot}140_2$ | $1{\cdot}152_3$ | $1{\cdot}145_0$ |
| Fe–C (mean) | $1{\cdot}822_3$ $(0{\cdot}001_4)$ | $1{\cdot}822_4$ | $1{\cdot}822_4$ | $1{\cdot}822_8$ | $1{\cdot}823_9$ | $1{\cdot}820_8$ | $1{\cdot}824_7$ | $1{\cdot}822_5$ |
| $\Delta$ | $0{\cdot}026_9$ $(0{\cdot}005_0)$ | $0{\cdot}028_2$ | $0{\cdot}028_5$ | $0{\cdot}027_6$ | $0{\cdot}013_5$ | $0{\cdot}032_9$ | $0{\cdot}015_2$ | $0{\cdot}031_3$ |
| Bond amplitudes (Å) | | | | | | | | |
| $u$(C–O) | $0{\cdot}024_9$ $(0{\cdot}007_7)$ | $0{\cdot}025_3$ | 0·0350* | $0{\cdot}024_9$ | $0{\cdot}024_7$ | $0{\cdot}027_9$ | $0{\cdot}022_6$ | $0{\cdot}025_4$ |
| $u$[Fe–C(1)] | $0{\cdot}049_5$ $(0{\cdot}003_4)$ | $0{\cdot}049_0$ | 0·0484* | $0{\cdot}044_3$ | $0{\cdot}049_7$ | $0{\cdot}048_9$ | $0{\cdot}050_3$ | $0{\cdot}049_2$ |
| $u$[Fe–C(2)] | $0{\cdot}048_3$ $(0{\cdot}003_4)$ | $0{\cdot}049_0$ | 0·0506* | $0{\cdot}043_2$ | $0{\cdot}049_1$ | $0{\cdot}047_4$ | $0{\cdot}049_6$ | $0{\cdot}047_8$ |
| Fe–C(1) | $1{\cdot}833_1$ $(0{\cdot}002_5)$ | $1{\cdot}833_7$ | $1{\cdot}833_8$ | $1{\cdot}833_8$ | $1{\cdot}829_3$ | $1{\cdot}833_9$ | $1{\cdot}830_8$ | $1{\cdot}835_0$ |
| Fe–C(2) | $1{\cdot}806_2$ $(0{\cdot}003_3)$ | $1{\cdot}805_5$ | $1{\cdot}805_3$ | $1{\cdot}806_2$ | $1{\cdot}815_8$ | $1{\cdot}801_0$ | $1{\cdot}815_6$ | $1{\cdot}803_8$ |
| $R_G$ | 0·1861 | 0·1861 | 0·1865 | 0·2099 | 0·2001 | 0·1945 | 0·1810 | 0·1855 |
| $R_D$ | 0·1284 | 0·1288 | 0·1296 | 0·1379 | 0·1300 | 0·1428 | 0·1156 | 0·1290 |

* Amplitude not refined.

Table 2. *Refinements carried out under various weighting schemes*

(*a*) Scheme II
(*b*) Scheme III
(*c*) Scheme IV
(*d*) 25 cm only (5 non-bonded $u_{ij}$ fixed)
(*e*) 50 cm only (6 non-bonded $u_{ij}$ fixed)
(*f*) Refinements of Almenningen, Haaland & Wahl.

| | *a* | *b* | *c* | *d* | *e* | *f* |
|---|---|---|---|---|---|---|
| C–O(mean) | 1·143$_1$ (0·001$_3$) | 1·144$_6$ (0·001$_4$) | 1·143$_7$ (0·001$_5$) | 1·138$_6$ (0·001$_6$) | 1·147$_9$ (0·003$_0$) | 1·147 (0·002) |
| Fe–C(mean) | 1·823$_7$ (0·001$_0$) | 1·823$_3$ (0·001$_1$) | 1·823$_7$ (0·001$_1$) | 1·827$_5$ (0·001$_3$) | 1·818$_9$ (0·002$_4$) | 1·827 (0·003) |
| $\Delta$ | 0·022$_4$ (0·004$_6$) | 0·026$_8$ (0·004$_7$) | 0·027$_5$ (0·004$_6$) | 0·017$_1$ (0·010$_5$) | 0·024$_0$ (0·007$_4$) | 0·012 (0·006) |
| Fe–C(1) | 1·832$_7$ (0·002$_3$) | 1·834$_1$ (0·002$_3$) | 1·834$_7$ (0·002$_3$) | 1·834$_3$ (0·004$_6$) | 1·828$_5$ (0·003$_9$) | 1·832 (0·005) |
| Fe–C(2) | 1·810$_3$ (0·002$_9$) | 1·807$_3$ (0·002$_9$ | 1·807$_2$ (0·002$_9$) | 1·817$_2$ (0·006$_2$) | 1·804$_5$ (0·004$_9$) | 1·820 (0·006) |
| $u$(C–O)$_{\mathrm{mean}}$ | 0·026$_8$ (0·005$_2$) | 0·025$_6$ (0·005$_8$) | 0·027$_4$ (0·005$_7$) | 0·030$_5$ (0·005$_0$) | 0·040$_1$ (0·019$_2$) | 0·0327 (0·0005) |
| $u$[Fe–C(1)] | 0·052$_2$ (0·002$_4$) | 0·050$_8$ (0·002$_7$) | 0·052$_2$ (0·002$_8$) | 0·056$_4$ (0·002$_7$) | 0·0564* | 0·057 (0·003) |
| $u$[Fe–C(2)] | 0·051$_1$ (0·002$_4$) | 0·049$_6$ (0·002$_6$) | 0·051$_0$ (0·002$_7$) | 0·055$_6$ (0·002$_6$) | 0·0556* | |
| $R_G$ | 0·1801 | 0·1836 | 0·1830 | 0·1480 | 0·1910 | |
| $R_D$ | 0·1385 | 0·1337 | 0·1200 | 0·1442 | 0·1198 | |
| $W_t$ (100 cm) | 0·25 | 0·63 | 5·29 | | | |
| $W_t$ (50 cm) | 0·50 | 0·66 | 0·37 | | | |
| $W_t$ (25 cm) | 1·00 | 1·00 | 1·00 | | | |

* Amplitude not refined.

Table 3. *Dependent distances and non-bonded amplitudes* (Å)

(*a*) Scheme I distances and standard deviations; refinement as in Table 1, col. (*a*).
(*b*) Scheme I non-bonded $u_{ij}$; refinement as in Table 1, col. (*a*).
(*c*) Scheme II non-bonded $u_{ij}$; refinement as in Table 2, col (*a*).
(*d*) Scheme III non-bonded $u_{ij}$; refinement as in Table 2, col. (*b*).
(*e*) Scheme IV non-bonded $u_{ij}$; refinement as in Table 2, col. (*c*).
(*f*) Refinement of Almenningen, Haaland & Wahl (1968).
(*g*) Calculated (spectroscopic) $u_{ij}$ at 298°K (Brunvoll, 1967).

| | *a* | *b* | *c* | *d* | *e* | *f* | *g* |
|---|---|---|---|---|---|---|---|
| Fe ····O(1) | 2·970$_9$ (0·002$_4$) | 0·055 (0·003) | 0·057 (0·002) | 0·056 (0·002) | 0·057 (0·002) | 0·055 (0·008) | 0·0503 |
| Fe ····O(2) | 2·947$_1$ (0·003$_1$) | 0·054 (0·003) | 0·056 (0·002) | 0·055 (0·002) | 0·055 (0·002) | 0·055 (0·008) | 0·0525 |
| C(1)···C(1′) | 3·167$_9$ (0·004$_1$) | 0·179 (0·032) | 0·162 (0·027) | 0·194 (0·034) | 0·127 (0·025) | 0·112 (0·015) | 0·1053 |
| C(1)···C(2) | 2·569$_8$ (0·001$_9$) | 0·103 (0·007) | 0·093 (0·005) | 0·097 (0·005) | 0·095 (0·006) | 0·123 (0·005) | 0·1490 |
| C(1)···O(1′) | 4·189$_8$ (0·003$_9$) | 0·153 (0·010) | 0·159 (0·009) | 0·152 (0·010) | 0·164 (0·012) | 0·149 (0·013) | 0·1284 |
| C(1)···O(2) | 3·466$_5$ (0·001$_9$) | 0·171 (0·005) | 0·168 (0·004) | 0·169 (0·005) | 0·159 (0·005) | 0·152 (0·010) | 0·1795 |
| C(2)···O(1) | 3·472$_6$ (0·001$_4$) | 0·171 (0·005) | 0·168 (0·004) | 0·169 (0·005) | 0·159 (0·005) | 0·152 (0·010) | 0·1818 |
| O(1)···O(1′) | 5·132$_3$ (0·004$_2$) | 0·171 (0·011) | 0·181 (0·011) | 0·176 (0·010) | 0·192 (0·011) | 0·231 (0·012) | 0·1718 |
| O(1)···O(2) | 4·177$_9$ (0·001$_9$) | 0·321 (0·030) | 0·301 (0·023) | 0·339 (0·029) | 0·294 (0·024) | 0·270 (0·026) | 0·2451 |
| C(2)···C(2′) | 3·593$_1$ (0·006$_2$) | 0·30 (0·21) | 0·26 (0·22) | 0·45 (0·16) | 0·27 (0·12) | 0·20 (0·10) | 0·0649 |
| C(2)···O(2′) | 4·729$_1$ (0·006$_0$) | 0·057 (0·013) | 0·071 (0·010) | 0·068 (0·011) | 0·073 (0·011) | 0·068 (0·010) | 0·0663 |
| O(2)···O(2′) | 5·861$_5$ (0·006$_2$) | 0·049 (0·018) | 0·067 (0·013) | 0·060 (0·014) | 0·066 (0·015) | 0·093 (0·027) | 0·0677 |

±0·005 Å, virtually the same value as that obtained in weighting scheme I.

*Refinement on single intensity curves*

As an extreme case of varying the $W_t$, refinements were carried out on the 25 cm data alone ($s=8·0$ to $30·0$ Å$^{-1}$) and also on the 50 cm data alone ($s=1·7$ to $13·5$ Å$^{-1}$). With these smaller amounts of data several of the amplitudes were not well defined, and were therefore fixed at values representative of those obtained in the previous refinements. The 25 cm results [Table 2, col. (*d*)] with 5 non-bonded amplitudes fixed provide a relatively small value of $\Delta$, 0·017 ± 0·011 Å, and a mean C–O bond length of 1·139 ± 0·002 Å which is considerably shorter than the corresponding values obtained in all the refinements on the full range of data.

Refinement on the 50 cm data with 6 non-bonded amplitudes and the two (Fe–C) bonded amplitudes fixed gave values for the bonded distance parameters [Table 2, col. (*e*)] in reasonable agreement with those obtained under weighting scheme I, and $\Delta=0·024$ ± 0·007 Å. In the 25 cm case the bonded amplitude values were markedly larger than those obtained in refinements on the whole data available. This is in accord with general experience (Hedberg & Iwasaki, 1964) that use of outer data alone often gives larger values for some of the more important amplitudes. Inclusion of the 100 cm data always yielded a (C–O) amplitude which is unreasonably small (though with a large estimated standard deviation). Refinement on either 25 cm data alone or 50 cm data alone gave values closer to the expected 0·035 Å.

## Discussion

In our refinements carried out on the full range of data, almost all of the different values obtained for $\Delta$ fell into the range $0·022 \le \Delta \le 0·030$ Å. The only exceptions to this are (i) the refinements where shrinkage corrections were omitted from the geometrical model, $\Delta=0·033$ Å, (ii) when shrinkage was refined, $\Delta=0·015$ Å and (iii) the refinement with all non-bonded amplitudes fixed at AHW's values, $\Delta=0·014$ Å. Alteration of the weighting scheme had little effect on the value of $\Delta$, and the constraint of the Fe–C amplitudes such that the equatorial bonds had the smaller amplitude [Table 1, col. (*c*)] had no effect either. Significance tests (carried out under weighting scheme I only) lead to 99·5% confidence limits of $0·013 \le \Delta \le 0·042$ Å, and the refinements under the other weighting schemes give us no reason to doubt these limits. If we take our best value of $\Delta$ as 0·027 ± 0·005 Å, the difference between this and AHW's 0·012 ± 0·006 Å is 0·015 ± 0·008 Å, in the 'not significant' range (Cruickshank, 1949). We find further that when our outer data are emphasized the values of $\Delta$ obtained decrease

Table 4. *Least squares correlation matrix multiplied by* 1000

Elements are 1000 $\varrho_{ij}$ ; $\varrho_{ij} = M_{ij} / \sigma_i \sigma_j$ where **M** is the variance-covariance matrix.

$U_1 = U(\text{C–O})$, $U_2 = U(\text{Fe–C})$, $U_4 = U(\text{Fe}\cdots\text{O})$ .

$U_6$ to $U_{15}$ are the remaining non-bonded amplitudes in the order of table 3. $U_3$, $U_5$ and $U_{10}$ are not included since each of these amplitudes is refined as a function of the preceding amplitude.

| C–O | Fe–C | $\Delta$ | $U_1$ | $U_2$ | $U_4$ | $U_6$ | $U_7$ | $U_8$ | $U_9$ | $U_{11}$ | $U_{12}$ | $U_{13}$ | $U_{14}$ | $U_{15}$ | $K_1$ | $K_2$ | $K_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1000 | −631 | 11 | −110 | −73 | −8 | 406 | 81 | −22 | −41 | −56 | 115 | 223 | 10 | −20 | −71 | −77 | −194 |
| −631 | 1000 | 74 | 19 | −53 | −13 | 17 | 112 | 1 | −24 | −48 | 30 | 96 | −18 | 5 | 29 | −67 | 74 |
| 11 | 74 | 1000 | −4 | −209 | −180 | 327 | 19 | −404 | 418 | 2 | 315 | 109 | 97 | 21 | −6 | −22 | −9 |
| −110 | 19 | −4 | 1000 | 270 | 311 | −55 | 18 | 80 | 72 | 50 | −62 | −96 | 38 | 50 | 20 | 316 | 425 |
| −73 | −53 | −209 | 270 | 1000 | 529 | −114 | −37 | 228 | 19 | 84 | −172 | −177 | 35 | 71 | 150 | 566 | 657 |
| −8 | −13 | −180 | 311 | 529 | 1000 | 125 | 54 | 175 | 66 | 45 | −63 | −13 | 60 | 80 | 123 | 518 | 711 |
| 406 | 17 | 327 | −55 | −114 | 125 | 1000 | 16 | −234 | 347 | −105 | 410 | 523 | 91 | 7 | 23 | −71 | −55 |
| 81 | 112 | 19 | 18 | −37 | 54 | 16 | 1000 | 6 | 29 | −23 | −23 | −17 | 1 | −2 | −45 | −142 | 63 |
| −22 | 1 | −404 | 80 | 228 | 175 | −234 | 6 | 1000 | −415 | 129 | −675 | −203 | −240 | 12 | 58 | 234 | 166 |
| −41 | −24 | 418 | 72 | 19 | 66 | 347 | 29 | −415 | 1000 | 46 | 206 | −172 | 96 | 21 | 70 | 72 | 151 |
| −56 | −48 | 2 | 50 | 84 | 45 | −105 | −23 | 129 | 46 | 1000 | −228 | −220 | 151 | −81 | 63 | 134 | 79 |
| 115 | 30 | 315 | −62 | −172 | −63 | 410 | −23 | −675 | 206 | −228 | 1000 | 684 | 270 | 12 | −101 | −194 | −107 |
| 223 | 96 | 109 | −96 | −177 | −13 | 523 | −17 | −203 | −172 | −220 | 684 | 1000 | 125 | 1 | −188 | −258 | −150 |
| 10 | −18 | 97 | 38 | 35 | 60 | 91 | 1 | −240 | 96 | 151 | 270 | 125 | 1000 | −38 | −25 | 12 | 91 |
| −20 | 5 | 21 | 50 | 71 | 80 | 7 | −2 | 12 | 21 | −81 | 12 | 1 | −38 | 1000 | 30 | 80 | 104 |
| −71 | 29 | −6 | 20 | 150 | 123 | 23 | −45 | 58 | 70 | 63 | −101 | −188 | −25 | 30 | 1000 | 168 | 156 |
| −77 | −67 | −22 | 316 | 566 | 518 | −71 | −142 | 234 | 72 | 134 | −194 | −258 | 12 | 80 | 168 | 1000 | 534 |
| −194 | 74 | −9 | 425 | 657 | 711 | −55 | 63 | 166 | 151 | 79 | −107 | −150 | 91 | 104 | 156 | 534 | 1000 |

Table 5. *Analysis of variance*

| Distance | U′wU | U′wU/I′wI | $N$ | U′wU/$N$ | $R_G$ | $R_D$ | Correlation |
|---|---|---|---|---|---|---|---|
| 100 cm | 1·3460 | 0·04111 | 166 | 0·00811 | 0·2027 | 0·1146 | 0·50000 |
| 50 cm | 18·6593 | 0·03952 | 189 | 0·09873 | 0·1988 | 0·1322 | 0·50000 |
| 25 cm | 9·2110 | 0·02638 | 151 | 0·06100 | 0·1624 | 0·1576 | 0·49996 |

[Table 2, columns (*a*), (*d*), (*c*)]. AHW refined on a single composite intensity curve extending from $s=1$ to 48 $Å^{-1}$. This procedure in effect gives higher weight to the outer data than do our refinements, so that part of the change in $\Delta$ is presumably caused by differences in the refinement procedure and in the range of $s$ experimentally studied. There appears to be a systematic difference between C–O(mean) and between Fe–C-(mean) values in the two sets of results, amounting to about 2 parts per thousand. This is of the order of the combined uncertainties in the accelerating voltages of the instruments. When possible systematic errors are included, we obtain C–O(mean) $= 1{\cdot}145 \pm 0{\cdot}003$ Å, Fe–C(mean) $= 1{\cdot}822 \pm 0{\cdot}003$ Å.

In all other respects the correspondence between the present results and those of AHW is very good indeed. AHW obtain a value of $u$(C–O) which is very much better defined and closer to the spectroscopic value, a consequence of their more extensive data at high $s$. The agreement for the other amplitudes is satisfactory (Tables 1, 2 and 3), and both sets of results show reasonable correspondence with the calculated amplitudes of Brunvoll (1967). The cases where agreement is least good and where our values of the amplitudes are most strongly dependent on the weighting scheme are (*a*) C(1)$\cdots$C(1′), C(2)$\cdots$C(2′) and O(2)$\cdots$O(2′); these all give rise to weak peaks in $P(r)/r$, the former two being also overlapped by the strong Fe$\cdots$O(1), Fe$\cdots$O(2), C(1)$\cdots$O(2) and C(2)$\cdots$O(1) peaks, (*b*) O(1)$\cdots$O(2), where the calculated amplitude is very large (0·245 Å). The detailed agreement between the present work and the Norwegian results is particularly gratifying in view of the complexity of this electron diffraction problem and the large number of parameters refined.

A direct comparison with the results of Davis & Hanson (1965, 1967) is less easy to make, since these authors provide no information in either of their communications concerning the values of the non-bonded amplitudes and whether these were refined or not. Since we have shown that when the non-bonded amplitudes are fixed at other than our refined values [Table 1, col. (*e*)] $\Delta$ may change appreciably, this point is of critical importance. We must presume that Davis & Hanson did not include shrinkage corrections in their calculations, although they make no specific comment on this either. Without shrinkage [Table 1, col. (*f*)] we obtain $\Delta = 0{\cdot}033 \pm 0{\cdot}005$ Å, which is not inconsistent with the $\Delta = 0{\cdot}049 \pm 0{\cdot}020$ Å obtained by Davis & Hanson (1967). Their Fe–C(mean) of $1{\cdot}823 \pm 0{\cdot}001_4$Å is in accordance with our $1{\cdot}822 \pm 0{\cdot}003$ Å and AHW's $1{\cdot}827 \pm 0{\cdot}003$ Å. For C–O(mean) they obtain 1·136 $\pm 0{\cdot}001_5$ Å, while we find $1{\cdot}145 \pm 0{\cdot}003$ Å and AHW $1{\cdot}147 \pm 0{\cdot}002$ Å. Part of this discrepancy may be due to their omission of the large shrinkage in the Fe$\cdots$O distances, calculated as 0·0074 Å for Fe$\cdots$O(1) and 0·0044 Å for Fe$\cdots$O(2) at 25 °C: the omission of shrinkage [Table 1, col. (*f*)] causes our Fe–C(mean) to fall to 1·821 Å and C–O(mean) to 1·140 Å.

While Donohue & Caron (1966, 1967) have made some pertinent comments regarding the refinement of bonded and non-bonded amplitudes, we have shown that after all amplitudes are successfully refined there remains a very high probability that the equatorial Fe–C bond length in iron pentacarbonyl is longer than the axial bond length by a small amount. There seems no good reason for choosing between our best value [Table 1, col. (*a*)] and that of AHW, which are in essential agreement. It seems very unlikely that the true value of $\Delta$ lies outside the range 0·038 Å to 0·0 Å, *i.e.* two standard deviations outside the respective values. If we take these limits as the 99% confidence interval, we conclude that the best value of $\Delta$ is $0{\cdot}019 \pm 0{\cdot}008$ Å.

The data (Hanson, 1962) used in both crystal structure refinements were collected from 3 zones each at a different temperature and they are not extensive for a monoclinic space group (317 observed reflexions). With data of higher quality the standard deviations obtained in these refinements could probably be improved. At present it can only be said that the mean Fe–C bond length in the solid, $1{\cdot}79_5 \pm 0{\cdot}02$ Å, is compatible with the gas-phase results, as Donohue & Caron (1967) have pointed out.

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