Accurate Determination of a Classic Structure in the Metal Carbonyl Field: Nonacarbonyldi-iron

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An equidimensional single crystal of $Fe_2(CO)_9$ has been used to reinvestigate the molecular structure. The results confirm all the main qualitative features originally reported by Powell and Ewens, and provide the level of accuracy needed for comparison with other structures and for molecular orbital calculations. The molecular symmetry is $C_{3h}(\bar{6})$, but there is little deviation from the higher symmetry $D_{3h}(\bar{6}m2)$. The important molecular dimensions, with their estimated standard deviations in parentheses are: Fe–Fe, 2·523(1) Å; Fe–C (terminal), 1·838(3) Å, Fe–C (bridge), 2·016(3) Å; C–O (terminal), 1·156(4) Å; C–O (bridge), 1·176(5) Å; C(term.)–Fe–C(term.), 96·1(1)°; Fe–C(bridge)–Fe, 77·6(1)°; Fe–C–O (term.), 177·1(3)°. Space group: $P6_3/m$. a = 6·436(1) Å, c = 16·123(2) Å, V = 578·4(2) Å^3, Z = 1. Of 1064 unique reflections measured with a counter diffractometer, 604 with intensity at least three times the e.s.d. were used to refine the structure (34 parameters) to final discrepancy indices of 0·040 (unit weighted data) and 0·050 (weighted data).

NONACARBONYLDI-IRON, $Fe_2(CO)_9$, was the first polynuclear metal carbonyl [and only the third, after $Ni(CO)_4$ and $Fe(CO)_5$, of all metal carbonyls] to be discovered.[1] Its preparation constituted the first instance of photochemical generation of a polynuclear species from a simple mononuclear precursor. It was the first polynuclear metal carbonyl to be structurally characterized by X-ray crystallography[2,†] and it was this investigation that revealed the existence of the bridging carbonyl, a structural unit now recognized as enormously important. Finally, it was $Fe_2(CO)_9$ that constituted the model system with which Sheline and Pitzer first showed that infrared spectra could be used to detect the presence of bridging CO groups.[4]

In view of all this it is ironic that the structure of this molecule should have remained one of those least accurately known, while the structures of hundreds of other metal carbonyl species, the majority of which are of incomparably less significance, are now known quite accurately. There has been, of course, a simple, practical reason for this. Nonacarbonyldi-iron crystallizes in the form of extremely thin plates; flakes would perhaps be a more descriptive appelation. The crystal used by Powell and Ewens, for example, was a hexagonal plate measuring 0·2 mm in mean diameter but only 0·02 mm in thickness. Powell and Ewens were unable to obtain any data for crystals mounted along the c axis (the direction of the short physical dimension). Undoubtedly this problem has discouraged attempts to reinvestigate the structure. There seemed no way to overcome the basic problem of unfavourable crystal shape since the general insolubility of $Fe_2(CO)_9$ has frustrated efforts to recrystallize it, beginning with the earliest such effort by Dewar and Jones in 1905.

Through a series of occurrences outlined below it became our good fortune to possess a well-formed equidimensional crystal of $Fe_2(CO)_9$, and an accurate redetermination of the structure was therefore undertaken.

EXPERIMENTAL

Crystal Preparation.—In the course of studies of the reactions of $Fe_2(CO)_9$ we fortuitously found that large, equidimensional crystals could sometimes be obtained from tetrahydrofuran solutions. Unfortunately, when such crystals were deliberately grown in capillaries [along with crystals of $Fe_3(CO)_{12}$ and an as yet unidentified red compound] they disintegrated in the solvent atmosphere too quickly. A search was then made in a bottle of di-iron nonacarbonyl purchased from Pressure Chemical Company. Amongst thousands of the usual, unsuitable sort of crystals, one very good crystal measuring 0·20 × 0·20 × 0·25 mm was found and was used to collect an extensive set of data. Continued searching has not located another such crystal.

Collection of X-*Ray Data.*—Preliminary examination of the crystal and data collection were performed on a Syntex computer-controlled diffractometer equipped with a graphite-crystal incident-beam monochromator. The unit cell was shown to be the same as the hexagonal unit cell found by Powell and Ewens.[2] Cell constants (22 °C) obtained from a least-squares refinement of the setting angles for fifteen strong reflections are: a = 6·436(1), c = 16·123(2) Å, and V = 578·4(2) Å^3. These may be compared with those reported by Powell and Ewens: a = 6·45 Å and c = 15·98 Å. The width at half-height for ω scans of several strong reflections was 0·15°.

Intensity data were collected at 22 °C with Mo-K_α radiation using the θ—2θ scan technique and a variable scan rate of 2·0—24·0°/min depending on the intensity of the reflection. A symmetrical scan range of 2θ(Mo-$K_{\alpha1}$) $-$1·0° to 2θ(Mo-$K_{\alpha2}$) $+$1·0° was used to measure 1064 unique reflections (hkl) up to a maximum 2θ of 70°. Three standard reflections were measured after every 100 reflections to check on crystal and electronic stability. No trends in the standards were observed. An absorption correction was not made in view of the small variation in transmission factors (56 ± 3%) through the extreme directions of the crystal during data collection. In the refinement of the structure 604 reflections having $F_o^2 > 3\sigma(F_o)^2$ were used. The parameter p used in the calculation of standard deviations[5] was set equal to 0·06.

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† This was truly the first one for *any* metal carbonyl since earlier study of the Group VI hexacarbonyls[3] did not involve genuine, *ab initio* structure determination.

[1] J. Dewar and H. O. Jones, *Proc. Roy. Soc.* (*London*), 1905, **A76**, 558.

[2] H. M. Powell and R. V. G. Ewens, *J. Chem. Soc.*, 1939, 286.

[3] W. Rudorff and V. Hofmann, *Z. phys. Chem.* (*Leipzig*), 1935, **28**, 351.

[4] R. K. Sheline and K. S. Pitzer, *J. Amer. Chem. Soc.*, 1950, **72**, 1107.

[5] F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organometallic Chem.*, 1973, **50**, 227.

Refinement of the Structure.[6]—Atomic positional parameters derived from Powell and Ewens two-dimensional *X*-ray study were used directly in the refinement of the structure. The space group was tentatively assumed to be $P6_3/m$ as determined in the two-dimensional study. Three cycles of full matrix least-squares refinement employing isotropic temperature factors converged to the following discrepancy indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0{\cdot}076$ and $R_2 = [\Sigma w(|F_o| - |F_o|)^2/\Sigma w|F_c|^2]^{\frac{1}{2}} = 0{\cdot}110$. The terms $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes and w is the weighting factor, $4F_o^2/\sigma^2$, where σ is the e.s.d. of F_o^2. Three additional least-square cycles, in which all atoms were refined anisotropically, converged to give the final discrepancy indices of $R_1 = 0{\cdot}040$ and $R_2 = 0{\cdot}050$ with no parameter shift in the last cycle greater than 0·01 times the e.s.d. for that parameter. The error in an observation of unit weight is 1·15.

Attempted refinement in the non-centric space group, $P6_3$, resulted in very large correlation coefficients between atoms related by the mirror plane in space group $P6_3/m$, but produced no improvement in the discrepancy indices. This confirms that the original choice of $P6_3/m$ is the correct space group.

TABLE 1

Positional and anisotropic thermal parameters with their estimated standard deviations [a]

Atom	x	y	z	β_{11} [b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	1/3	2/3	0·17175(3)	0·0188(2)	β(1,1)	0·0016(1)	β(1,1)/2	0	0
O(1)	0·3310(7)	0·0895(5)	1/4	0·039(1)	0·019(1)	0·003(1)	0·019(1)	0	0
O(2)	0·3441(5)	0·2817(5)	0·0747(1)	0·050(1)	0·034(1)	0·003(1)	0·028(1)	−0·001(1)	−0·002(1)
C(1)	0·3320(8)	0·9098(7)	1/4	0·019(1)	0·017(1)	0·003(1)	0·009(1)	0	0
C(2)	0·3380(6)	0·4243(5)	0·1133(2)	0·024(1)	0·024(1)	0·002(1)	0·012(1)	−0·000(1)	0·000(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all other tables. [b] The anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}h + 2\beta_{23}kl)]$.

Atomic scattering factors were taken from the International Tables.[7] Anomalous dispersion effects were included in the calculated structure factors for iron using $\Delta f'$ and $\Delta f''$ values given by Cromer and Liberman.[8] No systematic trends were found in the data as a function of $\lambda^{-1}\sin\theta$, $|F_o|$, Miller indices, or reflection number.

The atomic co-ordinates, anisotropic thermal parameters, and estimated standard deviations are given in Table 1. Root-mean-square amplitudes of thermal vibration are given in Table 2. A list of observed and calculated structure factors appears in Supplementary Publication No. SUP 20886 (3 pp.) *

TABLE 2

Root-mean-square amplitudes of thermal vibration (Å)

Atom	Min.	Intermed.	Max.
Fe	0·143(1)	0·172(1)	0·172(1)
O(1)	0·140(5)	0·202(4)	0·248(4)
O(2)	0·175(3)	0·223(4)	0·283(3)
C(1)	0·165(5)	0·173(5)	0·190(5)
C(2)	0·163(3)	0·189(4)	0·195(4)

Table 3 gives various significant dimensions of the molecule. In view of the very small e.s.d.'s for bond distances, corrections for the effect of thermal motion were deemed necessary. Only for the C–O distances were these appreciable. Both uncorrected and corrected distances are listed in Table 3; only the corrected ones are used in discussion.

DISCUSSION

The structure is qualitatively exactly as described by Powell and Ewens in 1939. We have confirmed their choice of space group, *viz.*, the centric $P6_3/m$ rather than the acentric $P6_3$, both of which are consistent with the systematic extinctions. Therefore, the molecule has $C_{3h}(\bar{6})$ symmetry.

It is generally assumed that the full symmetry of the molecule, if it were unperturbed by intermolecular contacts, would be $D_{3h}(\bar{6}m2)$, and indeed the deviations from this are but slight. The relative rotational orientation of the triangular sets of terminal and bridging carbon atoms differs by only 0·7(2)° from that corresponding to perfect staggering, and the oxygen atoms lie only 0·030(12) and 0·019(6) Å, for the terminal and planar ones,

TABLE 3

Intramolecular bond lengths (Å) and angles (°)

Distances:	Uncorr. [b]	Corr. [b]		Uncorr. [b]	Corr. [b]
Fe–Fe′ [a]	2·523(1)		C(1)–O(1)	1·160(5)	1·176(5)
Fe–C(1) [c]	2·013(3)	2·016(3)	C(2)–O(2)	1·127(4)	1·156(4)
Fe–C(2) [c]	1·835(3)	1·838(3)			

Angles:

Fe–Fe′–C(2)	120·9(1)
Fe–C(1)–Fe	77·6(1)
C(2)–Fe–C(2)′	96·1(1)
C(1)–Fe–C(1)′	84·9(1)
Fe–C(1)–O(1)	141·2(1)
Fe–C(2)–O(2)	177·1(3)

Distances from planes:

Plane	Atom	Distance from plane
I C(1), C(1)′, C(1)″	Fe	1·262(1)
II C(2), C(2)′, C(2)″	Fe	0·941(3)
III Fe–Fe–C(2)	O(2)	0·019(6)
IV Fe–Fe–C(1)	O(1)	0·030(12)

Dihedral angle:

Plane III—Plane IV	179·3(2)

[a] Primes indicate symmetry related atoms. [b] Uncorr. and corr. refer to the omission and inclusion, respectively, of a correction for the effect of thermal motion on the apparent distance. A riding model (O on C, C on Fe) was used. [c] (1) and (2) refer to bridging and terminal CO groups, respectively.

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[6] Computer programs used in data reduction and in the refinement of the structure were as follows: DATARED by Frenz was used for data reduction. NUCLS, a full-matrix least-squares program by Ibers and Doedens, closely resembles Busing and Levy's ORFLS program; the function minimized in the refinement is $\Sigma w(|F_o| - |F_c|)^2$. Atomic distances, angles, and errors were calculated using program ORFFE by Busing, Martin, and Levy as modified by Brown, Johnson, and Thiessen.

[7] D. T. Cromer and J. T. Waber, 'International Tables for *X*-Ray Crystallography,' vol. IV, in preparation.

[8] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1971, **53**, 1891.

respectively, from the appropriate vertical planes defined by the carbon and iron atoms.

The structure as previously reported had certain quantitative features which were, apparently, inconsistent with currently accepted patterns for metal carbonyl structures. Of course, a realistic estimate of the probable uncertainties would have suggested that these apparent inconsistencies were not to be taken seriously, but nevertheless, it is gratifying to find that they do indeed vanish in the accurate structure. Thus, the Fe–C (bridge) bonds are significantly longer (by about 0·18 Å) than the Fe–C (terminal) bonds, as would be expected both on theoretical grounds and empirically from consideration of many other structures. Also, the previously reported Fe–Fe distance, 2·46 Å, seemed surprisingly short when compared with the distances now known for many other bi- and poly-nuclear iron carbonyl species, and indeed, it is. The actual distance is 2·523 Å, a more reasonable value.

A notable feature of this structure is the small angle at the bridging carbon atom. A survey of the literature revealed angles from 81·0(3)° [9] to 89(1)°; [10] most commonly, these angles are close to 84°. The angle of 77·6(1)° has the record low value by a margin more than 3°. This very low value serves further to emphasize the point, recently stressed by Braterman,[11] that bridging CO groups in metal carbons are fundamentally different from the carbonyl groups in organic compounds such as ketones and even from RC(O)M groups, where the angles at the carbon atom are typically around 120° and may be as high as 124°.[12]

In view of the accuracy with which this highly symmetrical structure is now known, nonacarbonyldi-iron would appear to be an attractive subject for a molecular orbital investigation aimed at exposing the essential features of bonding in carbonyl bridges. Such an investigation has been undertaken in the CNDO approximation.

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[9] M. R. Churchill and P. H. Bird, *Inorg. Chem.*, 1969, **8**, 1941.

[10] F. A. Cotton and M. D. LaPrade, *J. Amer. Chem. Soc.*, 1968, **90**, 2026.

[11] P. S. Braterman, *Structure and Bonding*, 1972, **10**, 57.

[12] F. A. Cotton, B. A. Frenz, and A. Shaver, *Inorg. Chim. Acta*, 1973, **7**, 161.