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An Electron Diffraction Study of Trismethylenemethane Iron Tricarbonyl

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The electron scattering pattern from gaseous trismethylenemethane iron tricarbonyl has been recorded from 2.50 $Å^{-1}$ to 38.75 $Å^{-1}$. The molecular structure was found to be C_{3v} with a staggered arrangement of the ligands. The bond distances, valence angles, and root mean square amplitudes are given in Table 1.

The synthesis of the novel compound trismethylenemethane iron tricarbonyl was reported by Emerson, Ehrlich, Giering and Lauterbur in 1966.[1] At temperatures above −60°C the proton magnetic resonance spectrum of the compound consists of a sharp singlet. This indicates that all hydrogen atoms are equivalent, *i.e.* that the molecular symmetry is C_{3v}.[1] There are two molecular models with this symmetry. One of them, the staggered model in which the six carbon atoms form a trigonal antiprism about the iron atom, is shown in Fig. 1. The other model is eclipsed; it can be obtained from the staggered model by rotating the $Fe(CO)_3$ fragment 60° about the threefold symmetry axis.

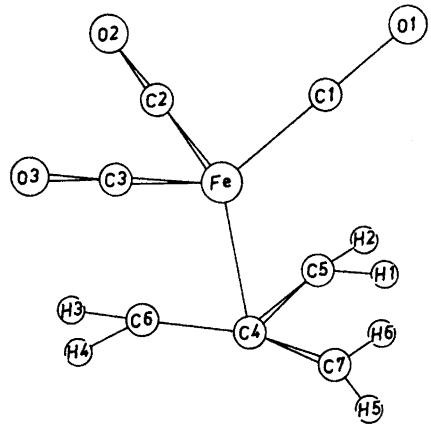

Fig. 1. The molecular structure of trismethylenemethane iron tricarbonyl.

However, the possibility that the hydrogen atoms are rendered NMR-equivalent through rapid exchange between less symmetric forms cannot be ruled out.

Cand. real. Harald Møllendal has attempted to record the MW spectrum of $(CH_2)_3CFe(CO)_3$,[2] but without success. Evidently the dipole moment must be quite small.

Table 1. Structure parameters with standard deviations of $(CH_2)_3CFe(CO)_3$. The bond distances are given as $r_g(1)$.[12] The standard deviations include the uncertainty in the electron wavelength. The angles have not been corrected for shrinkage.

	R (Å)	u (Å)
Fe—C1	1.810(0.003)	0.056(0.003)
Fe—C4	1.938(0.005)	0.033(0.009)
Fe—C5	2.123(0.005)	0.066(0.005)
C1—O1	1.153(0.002)	0.031(0.001)
C4—C5	1.437(0.003)	0.055(0.002)
C5—H1	1.111(0.009)	0.081(0.013)
O1···O2	4.515(0.055)	0.25 (0.36)
O1···C2	3.713(0.041)	0.24 (0.11)
O1···Fe	2.963(0.003)	0.063(0.004)
O1···C4	4.242(0.026)	0.157(0.045)
O1···C5	3.762(0.030)	0.13 (0.14)
O1···C6	5.007(0.011)	0.095(0.011)
O1···H1	3.367(0.044)	0.14 (0.28)
O1···H2	4.446(0.045)	0.20 (2.5)
O1···H3	5.584(0.028)	0.13 (2.5)
C1···C2	2.758(0.034)	0.19 (0.38)
C1···C4	3.220(0.021)	0.102(0.029)
C1···C5	2.883(0.024)	0.103(0.049)
C1···C6	3.871(0.009)	0.097(0.014)
C1···H1	2.781(0.039)	0.12 (0.37)
C1···H2	3.589(0.038)	0.10 (0.37)
C1···H3	4.456(0.028)	0.22 (5.3)
Fe···H1	2.729(0.029)	0.16 (0.33)
C4···H1	2.230(0.031)	0.062(0.029)
C5···C6	2.418(0.005)	0.061(0.006)
C5···H3	2.710(0.043)	0.11 (0.15)
C5···H4	3.444(0.017)	0.089(0.060)
H1···H2	1.867(0.052)	0.12[a]
H1···H3	3.820(0.045)	0.15[a]
H1···H4	4.394(0.044)	0.16[a]
H1···H6	2.528(0.095)	0.14[a]
∠C1—Fe—C4	118.4°(1.3°)	
∠C1—Fe—C2	99.2°(1.7°)	
∠Fe—C4—C5	76.4°(0.2°)	
∠C5—C4—C6	114.6°(0.2°)	
∠H1—C5—H2	113.4°(5.8°)	
β[b]	14.4°(5.1°)	
∠Fe—C1—O1	180.0°[a]	

[a] Assumed.
[b] β is the angle between the C4—C5 bond and the line bisecting the H1C5H2 angle.

EXPERIMENTAL AND CALCULATION PROCEDURE

The sample of $(CH_2)_3CFe(CO)_3$ was a gift from professor Emerson, and was used without further purification. The scattering pattern from the gas was recorded on the Oslo electron diffraction unit [3] with a nozzle temperature of 47 ± 5°C. Exposures were made with two nozzle to photographic plate distances, the two sets of plates thus obtained covered the diffraction ranges $s = 2$ Å^{-1} to 20 Å^{-1} and $s = 5$ Å^{-1} to 40 Å^{-1}. $s = (4\pi/\lambda)\sin(\theta/2)$ where λ is the electron wavelength and θ the diffraction angle.

Four plates from the first set and six plates from the second were photometered and read off at $\Delta s = 0.125$ Å^{-1} or $\Delta s = 0.250$ Å^{-1} intervals. The data were corrected and processed in the usual way.[4]

The resulting modified molecular intensity points from 2.50 Å^{-1} to 38.75 Å^{-1} are shown in Fig. 2. Below $s = 8.50$ Å^{-1} the point density is eight per Å^{-1}, above 8.50 Å^{-1} four points per Å^{-1}.

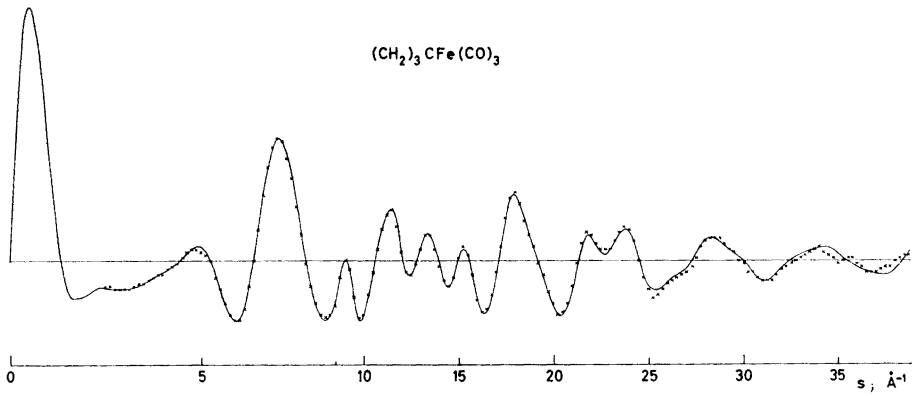

Fig. 2. Theoretical modified molecular intensity curve of $(CH_2)_3CFe(CO)_3$ with experimental values drawn in. Note that the s-scale is not uniform.

Theoretical curves were calculated from

$$I^{CC}(s) = \sum_{i \neq j} \frac{|f_i(s)| \cdot |f_j(s)|}{|f_C(s)|^2} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2)$$

$$= \sum_{i \neq j} g_{ij}/_{CC}(s) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\tfrac{1}{2}u_{ij}^2 s^2)$$

The sum extends over all atom pairs i,j in the molecule. R_{ij} is the internuclear distance, u_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)|\exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j. It has been computed for Fe, O, C, and H by the partial wave approximation with a program written by Peacher.[5] The scattering potentials of Fe, O, and C have been found by nonrelativistic Hartree-Fock-Slater computations.[6,7]

Radial distribution (RD) curves were obtained by Fourier inversion of experimental or theoretical intensity curves after multiplication with the artificial damping function $\exp(-ks^2)$.

The molecular structure was refined by least-squares calculations on the intensity data with a program written by Seip.

STRUCTURE ANALYSIS

A radial distribution (RD) curve obtained by Fourier inversion of the experimental intensity is shown in Fig. 3. In this curve the distance R_{ij} between atoms i and j is represented by a peak centered at $r=R_{ij}$. The area under the peak is roughly proportional to Z_iZ_j/R_{ij} where Z_i and Z_j are the

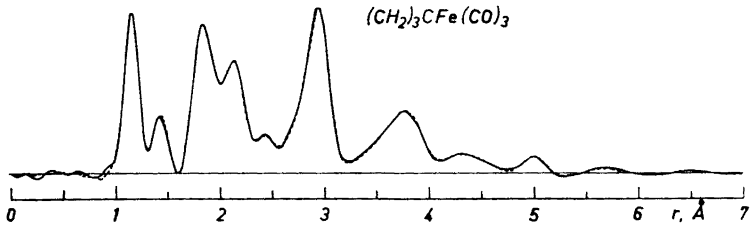

Fig. 3. Radial distribution curves of $(CH_2)_3CFe(CO)_3$. ——— experimental, - - - - - theoretical calculated from the parameters in Table 1. $k=0.0015$ Å^2.

atomic numbers. The halfwidth of the peak is determined by the root mean square variation of the distance, the vibrational amplitude, u_{ij}.

The experimental RD curve may be interpreted in the following way:

I. The peak at 1.1 Å is the sum of three peaks representing the three C—O bond distances and six peaks representing the six C—H bond distances.

II. The peak at 1.4 Å is the sum of three C—C bond distance peaks.

III. The peak at 1.8 Å is the sum of three Fe—C (carbonyl) bond distance peaks and the Fe—C4 (see Fig. 1) bond distance peak.

IV. The three distances Fe—C5, Fe—C6, and Fe—C7 are represented by the peak at 2.1 Å. The narrowness of this peak shows that the three distances must be equal to within a few hundreths of an Å. Hence the valence tautomerism discussed by Emerson *et al.*[1] can be ruled out; the molecular symmetry must be C_{3v}.

V. The small peak at 2.4 Å represents the three nonbonded distances C5···C6, C6···C7, and C5···C7.

VI. The peak at 2.9 Å is highly composite, but the main contribution is the three Fe···O distance peaks.

VII. The area under the peak at 5.0 Å corresponds to *three* O···C distances, and the area under the peak at 5.7 Å to *six* O···H distances. The peaks may therefore be assigned to the three distances of the type O1···C6 and to the six distances of the type O1···H3. These peaks show that the molecular conformation must be staggered; if it had been eclipsed there would have been *six* distances of type O1···C5 and *twelve* distances of type O1···H3, and the area under the corresponding peaks in the RD curve should have been twice as large.

VIII. The two peaks at 3.8 Å and 4.3 Å are highly composite consisting of peaks representing the remaining interatomic distances.

The molecular structure was refined by least-squares calculations on the intensity data under the assumption that the molecular symmetry is staggered

C_{3v} and that the Fe—C—O angles are 180°. It was not possible to refine all bond distances, valence angles and vibrational amplitudes simultaneously. The refinement was therefore alternated between the simultaneous refinement of all parameters except the H1—C5—H2 valence angle and the angle (β) between the C4—C5 bond and the line bisecting the H1—C5—H2 angle, and the simultaneous refinement of all bond distances and valence angles. In this manner the refinement converged to give the parameter values listed in Table 1. The standard deviations listed were obtained by carrying out a final cycle in the least-squares calculations in which all parameters were allowed to vary. The standard deviations include the uncertainty in electron wavelength. The angles have not been corrected for shrinkage.

A theoretical modified molecular intensity curve calculated from the parameters in the table is shown in Fig. 2, an RD curve in Fig. 3. The agreement between experimental and theoretical curves is very good.

DISCUSSION

The Fe—C (carbonyl) distance in trismethylenemethane iron tricarbonyl appears to be somewhat shorter than the *average* Fe—C distance in iron pentacarbonyl;[9] Fe—C=1.824 Å (0.003 Å). Accordingly the C—O distance seems to be a little longer than in $Fe(CO)_5$; C—O=1.146 Å (0.002 Å).

It may be noted that the four atoms to which C4 is bonded, all lie well above the plane through the atom perpendicular to the symmetry axis. If the C4 atom is to have the major lobe of a hybrid atomic orbital pointing towards the iron atom, the remaining three equivalent orbitals must be directed towards points below this plane. The C4—C5, C4—C6, and C4—C7 bonds may therefore be regarded as bent.[10]

The Fe—C4 distance is found to be significantly shorter than the distance from the iron atom to the four carbon atoms in the cyclobutadiene ring of tetraphenylcyclobutadiene iron tricarbonyl[11] 2.067 Å (0.012 Å), while the Fe—C5 distance is significantly longer. The Fe—C5 distance is so long that we believe it to be in the attractive region of the bond energy *versus* distance curve, and that the attraction is balanced by repulsion between Fe and C4 (this distance we believe to be in the repulsion part of the bond energy curve) and by the resistance of the C4—C5 bond to increased bending.

The modest size of the vibrational amplitudes of the distances O1···C5, O1···C6, C1···C5, and C1···C6 shows that the molecule is quite rigid. The barrier to internal rotation of the trismethylenemethane ligand against the rest of the molecule must be quite high.

After this study had been completed Churchill and Gold[13] have published a preliminary account of an X-ray diffraction investigation of $(CHPh)(CH_2)_2C{\cdot}Fe(CO)_3$, phenyltrimethylenemethane iron tricarbonyl. Their results are in excellent agreement with ours except that the carbon atom to which the phenyl group is attached appears to be bent one or two degrees further away from the iron atom.

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