

Nuclear Magnetic Resonance Spectrum of Oriented (Cyclobutadiene)iron Tricarbonyl¹

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Abstract: The geometry of the four-proton system in (cyclobutadiene)iron tricarbonyl has been determined from the proton magnetic resonance spectrum in liquid crystal solution. The observed spectrum is characteristic of a geometry with only two independent direct magnetic dipole coupling constants. The observed splittings do not quite fit those expected from a square geometry. The possibility of a rectangular proton configuration was considered. This geometry could be a result either of a stable structure in the isolated molecule or a distortion of a square structure by the nematic solvent. Using a computer simulation program, it was possible to fit the observed spectrum with a rectangle in which the ratio of unequal sides is 0.9977 ± 0.0045 . Assuming reasonable bond lengths and coplanarity of the carbon and hydrogen skeletons, this corresponds to a change of 0.5° in the C-C-H angle. At worst, this is a very small departure from square symmetry and represents a limit on the extent to which the proton geometry can be rectangular and still yield a spectrum consistent with experimental results. The alternative possibility of a proton configuration rotating rapidly in the asymmetric force field of the liquid crystal environment is also considered.

In 1956, Longuet-Higgins and Orgel² predicted the stability of complexes of cyclobutadiene with transition metal carbonyls. In 1965, Pettit³ reported a synthesis of the first stable cyclobutadiene complex, (cyclobutadiene)iron tricarbonyl, CIT (see Figure 1). The geometry of the cyclobutadiene system is unknown, and, for this reason, it is of interest to study the proton configuration. Analysis of the nmr spectra of molecules dissolved in a nematic liquid crystal solvent can lead to a determination of the anisotropic magnetic dipole coupling constant.⁴ Since the anisotropic dipole-dipole interaction is sensitive to interproton distances, it is possible to study the proton geometry by analysis of the nematic pmr spectrum.

1. Nematic Four-Spin Spectra

A method for analysis of nmr spectra of molecules in nematic solution has been developed by Saupe,⁴ and the nematic pmr spectrum of CIT was predicted assuming that the protons are in a square and a rectangular configuration. In both structures, the degree of orientation of the molecule (and therefore of the proton system) is given by a single parameter S_{33} which is defined as

$$S_{33} = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

where θ is the angle between the magnetic field and the molecular symmetry axis (see Figure 1). The brackets signify a time average of the angular function. The dipolar Hamiltonian for the four protons, modified for partial orientation in a liquid crystal matrix, is for a rectangle (in cps)

$$\mathcal{H}^{(1)} = \frac{\gamma^2 \hbar}{4\pi} S_{33} \sum_{i < j}^4 (3I_{zi}I_{zj} - \bar{I}_i \cdot \bar{I}_j) R_{ij}^{-3}$$

(1) Research supported in part through National Science Foundation Grant No. NSF-GP-3559.

(2) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

(3) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

(4) A. Saupe, *Z. Naturforsch.*, **19A**, 161 (1964).

where γ is the proton gyromagnetic ratio, and R_{ij} is the distance between nuclei i and j . For a square proton configuration, the Hamiltonian is

$$\mathcal{H}^{(1)} = \frac{\gamma^2 \hbar}{4\pi R^3} S_{33} \sum_{i < j}^4 (3I_{zi}I_{zj} - \bar{I}_i \cdot \bar{I}_j)$$

where R is the ortho internuclear distance. For both cases, the Zeeman Hamiltonian is

$$\mathcal{H}^{(0)} = -\frac{\gamma H_0}{2\pi} (1 - \sigma - 2S_{33}\Delta\sigma/3) \sum_{i=1}^4 I_{zi}$$

H_0 is the magnitude of the external field, σ is the isotropic average of the chemical shift tensor, and $\Delta\sigma$ is the difference between the chemical shift measured perpendicular and parallel to the four-proton plane. Symmetric eight- and ten-line spectra are predicted for the square and rectangular structures, respectively. The splittings and intensities for both cases are given in Table I. The center of symmetry of both spectra is given by

$$\nu = \frac{\gamma H_0}{2\pi} (1 - \sigma - 2S_{33}\Delta\sigma/3)$$

2. Experimental Section

The nematic pmr spectrum of CIT was obtained in a 25 mole % solution of 4,4'-di-*n*-hexyloxyazobenzene at 76° and is shown in Figure 2. It appears to be a symmetric eight-line multiplet. Tetramethylsilane was used as an internal reference. The measured splittings and intensities are given in Table II. Intensities were obtained with a Varian V-3521 integrator.

3. The Proton Geometry

(a) **Square Structure.** A visual examination of the spectrum (see Figure 2) would lead to the conclusion that the protons are in a square configuration since there are eight lines. Normalized to the smallest splittings (ΔS_4 and $\Delta\nu_4$), the four splittings are

Theoretical (Table Ia)	1:2.80944:4.6561:6.65611
Experimental (Table II)	1:2.699 \pm 0.107:4.8 \pm 0.17:6.493 \pm 0.25

It can be seen that, within experimental error, the observed splittings are not quite in the same ratio as the

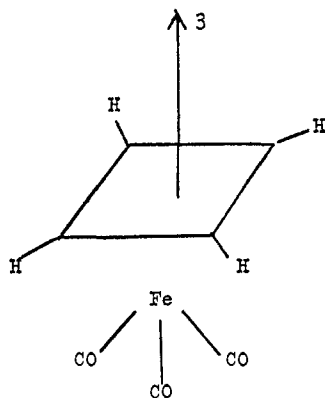


Figure 1. Molecular structure and direction of ordering axis (3) in (cyclobutadiene)iron tricarbonyl (CIT).

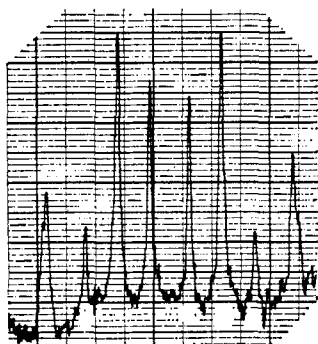
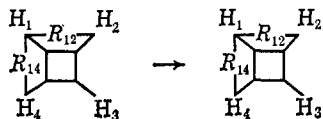


Figure 2. Nematic proton nmr spectrum of (cyclobutadiene)iron tricarbonyl.

theoretical splittings. The possibility that the spectrum actually consists of ten lines, two pairs of which are unresolved (*i.e.*, that the structure is a rectangle), was then considered. An estimate was made of the extent to which the proton structure could differ from a square (*i.e.*, become rectangular) and still fit the observed spectrum.

(b) **Rectangular Structure.** A possible continuous transition from square to rectangle may occur as



In this case, R_{12} becomes less than R_{14} . Since $B_{ij} = 3\gamma^2\hbar S_{33}/4\pi R_{ij}^3$, B_{12} becomes greater than B_{14} . If the proton chemical shift anisotropy is assumed to be negative, S_{33} must be positive to explain the relative position of the isotropic and nematic spectra. Then, since $R_{13} > R_{14} > R_{12}$, $B_{12} < B_{14} < B_{13}$. Using these inequalities, the transition of the stick-plot spectrum from square to rectangle was made and is shown in Figure 3. The only difference between the two spectra is that the innermost line pair, S_4 , in the "square" spectrum splits into the two "rectangular" line pairs, R_4 and R_5 . The separation between lines in the two pairs (on the same side of the center of symmetry) is given by (see Figure 3 and Table Ib)

$$\frac{1}{\pi}(B_{12} - B_{14}) = \frac{1}{2}(\Delta R_4 - \Delta R_5) \quad (1)$$

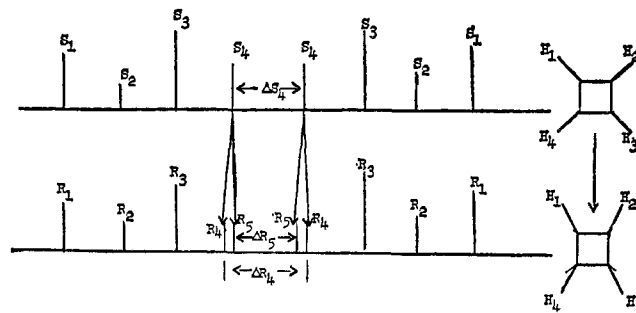


Figure 3. Change in nmr spectrum of four protons as structure changes from a square to a rectangle.

Experimentally, only four pairs of lines are obtained, and the half-width at half-height of the innermost pair is 3.0 cps. It was assumed that a line of the inner-

Table I. Theoretical Splittings and Intensities for Symmetric Four-Spin Spectra

Line pair ^a	Splitting	Intensity
a. Square Configuration: $B = (3\gamma^2\hbar/4R^3)S_{33}$		
S_1	$\Delta S_1 = \frac{B}{\pi} \left(2 + \frac{1}{2\sqrt{2}} \right)$	2
S_2	$\Delta S_2 = \frac{B}{\pi} \left(2 - \frac{1}{2\sqrt{2}} \right)$	1
S_3	$\Delta S_3 = \frac{B}{3\pi} \left[\left(2 + \frac{1}{2\sqrt{2}} \right)^2 + 8 \left(1 - \frac{2}{2\sqrt{2}} \right)^2 \right]^{1/2}$	3
S_4	$\Delta S_4 = \frac{B}{\pi} \left(\frac{1}{2\sqrt{2}} \right)$	2
b. Rectangular Configuration: $B_{ij} = (3\gamma^2\hbar/4R_{ij}^3)S_{33}$		
R_1	$\Delta R_1 = \frac{1}{\pi}(B_{12} + B_{13} + B_{14})$	2
R_2	$\Delta R_2 = \frac{1}{\pi}(B_{12} - B_{13} + B_{14})$	1
R_3	$\Delta R_3 = \frac{1}{3\pi} \{ (B_{12} + B_{13} + B_{14})^2 + 4[(B_{12} - B_{13})^2 + (B_{12} - B_{14})^2 + (B_{13} - B_{14})^2] \}^{1/2}$	3
R_4	$\Delta R_4 = \frac{1}{\pi}(B_{12} + B_{13} - B_{14})$	1
R_5	$\Delta R_5 = \frac{1}{\pi}(-B_{12} + B_{13} + B_{14})$	1

^a See Figure 3.

Table II. Observed Splittings and Intensities in the CIT Proton Nmr Spectrum

Splitting, cps	Intensity
$\Delta\nu_1 = 331.15 \pm 2.25$ (outermost pair)	2
$\Delta\nu_2 = 227.88 \pm 1.66$	1
$\Delta\nu_3 = 137.67 \pm 1.57$	3
$\Delta\nu_4 = 51.00 \pm 1.93$ (innermost pair)	2

most (observed) pair is actually a superposition of two "unresolved" lines. The separation between these two "unresolved" lines is given by eq 1. In order to place

a limit on this separation, it is necessary to find the maximum splitting which is possible between two overlapping lines (*i.e.*, R_4 and R_5) which are not resolved. For this purpose, a computer simulation program was used. The lines were given a Lorentzian shape and a half-width at half-height of 3.0 cps. It was found that the maximum separation consistent with experiment is 1.0 cps. Using (1), the following relation then holds

$$\frac{1}{\pi}(B_{12} - B_{14}) \leq 1.0 \text{ cps} \quad (2)$$

when $B_{12} - B_{14} = 0$, the proton configuration is a square. Thus, (2) places an upper limit on the distortion from a square structure. The separation between the outer pairs, R_1 and R_2 , is given by (see Table Ib)

$$\Delta R_1 - \Delta R_2 = \frac{2B_{13}}{\pi} \quad (3)$$

The splitting between the outermost pair is given by (see Table Ib)

$$\Delta R_1 = \frac{1}{\pi}(B_{12} + B_{13} + B_{14}) \quad (4)$$

Subtracting (3) from (4), the following is obtained.

$$\frac{1}{\pi}(B_{12} + B_{14}) = \Delta R_1 - \frac{1}{2}(\Delta R_1 - \Delta R_2) \quad (5)$$

To find the maximum departure from the square structure, $\frac{1}{\pi}(B_{12} - B_{14})$ is set equal to the limiting value of 1.0 cps. Using the observed splittings (Table II), eq 2-5 yield the following dipolar coupling constants (cps): $B_{12} = 440.64 \pm 4.18$, $B_{13} = 162.23 \pm 4.40$, $B_{14} = 437.50 \pm 4.18$. Under the above assumptions, these parameters fit the observed splittings.

A ratio of the interproton distances, R_{12}/R_{14} , is a meaningful estimate of the distortion of a square structure, since $R_{12}/R_{14} = 1$ for a square. Since $B_{ij} = 3\gamma^2\hbar S_{33}/4\pi R_{ij}^3$, this ratio can be obtained for the maximum distortion from a ratio of the above dipolar coupling constants.

$$\frac{R_{12}}{R_{14}} = \left(\frac{B_{14}}{B_{12}}\right)^{1/3} = 0.9977 \pm 0.0045$$

At worst, this represents a very small departure from square symmetry and places a limit on the extent to which the structure can depart from square symmetry and still fit the observed spectrum.

Other work points to a square structure for the carbon skeleton.⁵ A square configuration for the protons would then be reasonable. Assuming that this is the most stable geometry in the isolated molecule, the following explanation for the distortion is offered: a force is exerted on the C-H bonds as the molecule tumbles in the nematic solvent, and this squeezes the protons into a rectangular configuration. This explanation has been used on the distortion of the C-H bonds in the methyl groups of tetramethylsilane in the same solvent.⁶ The changes are of the same magnitude ($\sim 0.5^\circ$ change in the C-C-H angle). It is im-

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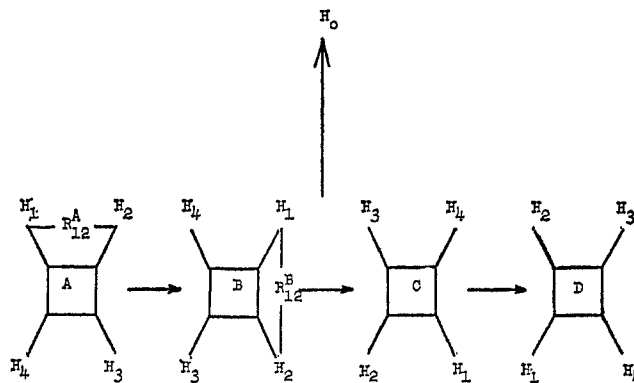


Figure 4. Rotation of the distorted cyclobutadiene ring in an asymmetric liquid crystal force field.

portant to note here that if the line widths were smaller, the maximum separation without resolution (eq 2) and the deviation from square structure would be smaller. It is expected that this would be the case with better sample temperature homogeneity.

(c) Rotationally Averaged Structure. The alternative possibility that the four-proton system is rotating rapidly in an asymmetric force field due to the liquid crystal environment was then considered. It is assumed that the anisotropy in distortion is such that the four protons are squeezed into a rectangle, the long side of which is parallel to the external field direction. The change in proton geometry as the cyclobutadiene ring rotates about its symmetry axis is shown in Figure 4. The four orientations shown are 90° apart in the angle between the external field direction and a given internuclear vector. It can be seen that the para internuclear distance (R_{13} and R_{24}) remains constant in magnitude during a rotation, while the ortho distance (R_{12} , R_{23} , R_{34} , and R_{14}) is averaged

$$\langle R_{\text{ortho}} \rangle = \frac{1}{2}(R_{12}^A + R_{12}^B)$$

This leads to a dipolar Hamiltonian modified for this type of distortion and rotational averaging

$$\mathcal{H}^{(1)} = (\gamma^2\hbar/4\pi S_{33}) \left[\langle R_{\text{ortho}}^{-3} \rangle \sum_{i < j} (3I_{zi}I_{zj} - \bar{I}_i \cdot \bar{I}_j) + R_{\text{para}}^{-3} \sum_{k < l} (3I_{zk}I_{zl} - \bar{I}_k \cdot \bar{I}_l) \right]$$

The first term inside the bracket is summed over all ortho nuclear pairs, and the second term over all para nuclear pairs. The spectrum resulting from this Hamiltonian is almost identical with that predicted for a square. The only difference is that the cube of the ratio of the para-to-ortho internuclear distance (derivable from the observed splittings) is not the same as that in a square. For the square, the following relation holds

$$\left(\frac{R_{\text{para}}}{R_{\text{ortho}}}\right)^3 = 2.828$$

From a least-squares analysis of the observed spectrum, the relation between the averaged distances is

$$\left\langle \left(\frac{R_{\text{para}}}{R_{\text{ortho}}}\right)^3 \right\rangle = 2.72 \pm 0.74$$

Without a more detailed knowledge of the force fields which produce the distortion, it is difficult to interpret the above result.

4. Scalar Nuclear Coupling

The scalar nuclear spin-spin coupling has been neglected in the preceding analysis. In a complete analysis, only the most intense line pair (S_3 or R_3 , Table I) is dependent on this parameter. Since the structure is very close to a square, and since the dependence on J_{ij} of the lines in the pair S_3 is much simpler than in the pair R_3 , only S_3 will be considered. When scalar coupling is included in the spin Hamiltonian the line pair, S_3 , is actually two pairs of lines, the separation between the lines in the two pairs (on the same side of the center of symmetry) being given by

$$\frac{1}{2}(\Delta S_{3a} - \Delta S_{3b}) = 3J_{12} = 3J_{\text{ortho}} \quad (\text{cps})$$

where ΔS_{3a} and ΔS_{3b} would be the splittings between the two pairs of lines if they could be resolved. Again, since the most intense lines appear to be singlets (see Figure 2), it is only possible to put a limiting value on their separation (without resolution), and hence on J_{ortho} . Using computer simulation (see section 3b), this was estimated to be 4.0 cps, so that $3J_{\text{ortho}} \leq 4.0$ cps and $J_{\text{ortho}} \leq 1.3$ cps. Because of line-width effects (see preceding section), it is likely that J_{ortho} is even

smaller. This result agrees with experimental observations by Pettit⁷ in the nmr spectrum of a derivative of CIT, in which $J_{\text{ortho}} = 0.0$ cps.

5. Proton Chemical Shift Anisotropy

The center of the nematic spectrum is 10.8 cps downfield from the isotropic spectrum. In order to estimate the proton chemical shift anisotropy, S_{33} must be known. A value for S_{33} can be calculated by the following procedure: (1) the observed splittings are matched to the theoretical square (see Table Ia) splittings to yield S_{33}/R^3 (this is reasonable since the observed spectrum is very close to that predicted for a square; see section 3a); (2) using C-C and C-H bond lengths of 1.4 and 1.1 Å, respectively, and assuming coplanarity of the carbon and hydrogen skeletons, the interproton distance, R , is found to be 2.96 Å. S_{33} then equals ± 0.02 . Using this value for S_{33} , a chemical shift anisotropy of ± 13 ppm is obtained. This is relatively large, being about the magnitude of shift anisotropies observed for acetylenic protons.⁸

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Energetics of the Ionization and Dissociation of $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, and $\text{ReMn}(\text{CO})_{10}$ ¹

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Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa. Received November 5, 1966

Abstract: The mass spectra of $\text{Re}_2(\text{CO})_{10}$, $\text{Mn}_2(\text{CO})_{10}$, and $\text{ReMn}(\text{CO})_{10}$ have been established and compared with the mass spectra of the monometal carbonyls. The electron-impact ionization potentials and the appearance potentials of the major fragment ions have been measured. These data are used to calculate specific and average bond dissociation energies for the ions. Metal-CO bond energies for $\text{Re}_2(\text{CO})_{10}^+$ are shown to be greater than those of $\text{Mn}_2(\text{CO})_{10}^+$. Metal-CO bond energies for $\text{ReMn}(\text{CO})_{10}^+$ are related to those observed for the Re_2 and Mn_2 compounds. A similar relative scale is predicted for the metal-CO bond energies of the neutral molecules. The calculated metal-metal dissociation energies (ev) of the neutral decacarbonyls and their ions to produce $\cdot\text{M}(\text{CO})_5$ and $\text{M}(\text{CO})_5^+$ are: Mn-Mn, 0.96, and $[\text{Mn-Mn}]^+$, 0.82; Re-Re, 2.22, and $[\text{Re-Re}]^+$, 2.08; Re-Mn, 2.67, and $[\text{Re-Mn}]^+$, 2.65. The ionization and dissociation mechanisms are discussed in terms of "isolated ionization" at one of the metal atoms in a dimetal carbonyl, and this model is tested by experimental observations.

Mass spectrometric studies of polynuclear carbonyls^{2,3} and derivatives^{4a} have been published recently. King² has worked primarily with the tri- and tetrametal carbonyls, while Preston and Reed^{4a} and Lewis *et al.*,^{4b} have concentrated their activities on the derivatives of dimetal carbonyls. No ionization

and appearance potential measurements are reported by these authors. Winter and Kiser³ report the ionization potentials of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$, and the appearance potentials of some fragment ions from these materials are used to calculate $\Delta H_f(\text{ion})$ values. Fragmentation patterns are also reported. These mass spectral patterns are important for the relationships to the quasi-equilibrium theory⁵ and for structural information.² However, the energetics of the various fragmentations are also of fundamental importance.

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1979.

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