JOURNAL OF MOLECULAR SPECTROSCOPY **154**, 355–360 (1992)

# The Microwave Spectrum of Cyclobutadiene Iron Tricarbonyl

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The rotational spectrum of cyclobutadiene iron tricarbonyl was measured using a Flygare–Balle-type microwave spectrometer. Twenty *a*-dipole transitions were measured in the 5–16 GHz range for this prolate symmetric-top molecule. A least-squares fit of the data to a distortable symmetric top Hamiltonian yielded $B = 961.9856(8)$ MHz, $D_J = 0.184(8)$ kHz, $D_{JK} = 1.20(3)$ kHz. These results indicate that the vibrationally averaged structure of the cyclobutadiene ring is square and perpendicular to the *a*-molecular axis.

## INTRODUCTION

Cyclobutadiene is a particularly elusive compound. The compound is only stable as a ligand of low valent transition metal compounds such as iron in cyclobutadiene iron tricarbonyl. Cyclobutadiene iron tricarbonyl ($CbFe(CO)_3$) was first synthesized by Emerson (*1*). Since then, there have been a number of speculations and experiments on the structure of uncoordinated cyclobutadiene (Cb) and Cb complexed as a ligand within a molecule (Cb*M*). Infrared matrix isolation studies (*2*) indicate that Cb is slightly rectangular with alternating single and double bonds. When cyclobutadiene is substituted with bulky *tert*-butyl groups, X-ray crystallographic data (*3*) show that the substituted Cb is rectangular. However, the rectangular geometry is probably a direct consequence of packing effects and the bulky substituents rather than the nature of Cb itself. The rectangular geometry observed in the matrix isolation studies (*2*) can be explained by the *pseudo-Jahn–Teller effect* which leads to a change in geometry toward lower symmetry in systems that have sets of degenerate orbitals that are not fully occupied (*4*). Therefore, it has been of interest, both experimentally and theoretically, to investigate the conditions for square vs rectangular geometry.

Although several experimental attempts have been made to characterize the structure of Cb in $CbFe(CO)_3$, none have clearly resolved this issue. Electron diffraction studies by Oberhammer and Brune (*5*) and Davis and Speed (*6*) have determined the basic geometry for $CbFe(CO)_3$. However, this technique is insensitive to asymmetries in the structure of the Cb ring. An earlier microwave study (*7*) indicates that $CbFe(CO)_3$ is a symmetric top. However, this previous study reported signals with 20–60 MHz half width. These low resolution measurements were not capable of observing small asymmetry splittings which would result from any departure from a symmetric top (square Cb) structure. In this paper we report the first pulsed beam Fourier transform microwave spectrum of $CbFe(CO)_3$ with a thousandfold increase in resolution over the earlier measurements.

## EXPERIMENTAL DETAILS

The $CbFe(CO)_3$ was synthesized in our lab following the basic procedure outlined by Pettit and Henery (*8*). Cis-3,4-dichlorocyclobutene (0.02 mol) (Fluka, Cat. No.

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* American Chemical Society Petroleum Research Fund Fellow.

0022-2852/92 $5.00

35635) and iron nonacarbonyl (0.05 mol) (Strem Chemical, Cat. No. 26-2640) were added to distilled benzene (20.0 ml), as a solvent, in a 100 ml round bottom flask. Reactants and products were handled in the inert atmosphere of a dry box. The reactants were refluxed at 55°C with continuous stirring for 1.5 hr. The reaction mixture gradually changed from an orange to a dark green solution with a noticeable evolution of carbon monoxide gas. The contents of the vessel were then filtered and the residue was washed with pentane and solvent was removed from the filtrate by enhanced evaporation under vacuum to afford the product as a dark green oil. Further purification of the product was achieved by distillation under vacuum. The dark green oil which contained $CbFe(CO)_3$ and iron pentacarbonyl with trace amounts of triirondodecacarbonyl was then transferred to a sample cell which could be fitted to the pulsed valve of our spectrometer.

The pulsed valve (General Valve 9-181-900 series) and sample were maintained at a constant temperature of 60°C with argon flowing over the sample and pulsed through the valve as described previously (*9, 10*). The spectrum was measured in the 4–16 GHz range using a pulsed beam Fourier transform microwave spectrometer (*11*) (PB-FTS) which is similar in design to the original Flygare–Balle (*12*) machine. The PB-FTS has had many modifications over the original design (*12*) to improve overall reliability, frequency range, and stability.

The $J = 5 \leftarrow 4$ transition was predicted to be near 9624 MHz based on the previous study (*7*). Under high resolution we observed a signal at 9619.7 MHz with closely spaced components with less than 40 kHz separation. Since $CbFe(CO)_3$ contains no nuclear quadrupole atom and natural distributions of other isotopic species are low, these components were assigned to the $J = 5 \leftarrow 4$ transition of $CbFe(CO)_3$ with splittings due to centrifugal distortion. Corresponding components of the $J = 3 \leftarrow 2$, through $J = 8 \leftarrow 7$ transitions were measured and are listed with their respective assignments in Table I. Signal strengths for single gas pulses ranged from 3/1 (S/N) for low-$J$ transitions to 1/1 for higher-$J$ transitions. Weak FID signals were detected at 17315 MHz due to $K$ components of the $J = 9 \leftarrow 8$ transition but were not included in the present analysis due to uncertainties in the line center measurements.

## RESULTS AND DISCUSSION

Spectroscopic parameters were obtained by fitting the measured frequencies in Table I to a prolate symmetric top Hamiltonian for which the transitions frequencies are given by

$$\nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2. \qquad (1)$$

The parameter values obtained from this analysis are shown in Table II. Since $K = 0$ and $K = 1$ components were not resolved for $J = 3 \leftarrow 2$, $4 \leftarrow 3$, $5 \leftarrow 4$, and $6 \leftarrow 5$ transitions, the calculated frequencies for $K = 0$ and $K = 1$ were averaged and fit to the corresponding observed line centers. The uncertainty of $B$, $D_J$, and $D_{JK}$ obtained from these calculations is well within the expected precision of microwave measurements. These parameters are compared to those of the earlier study (*7*) in Table II. The high resolution Fourier transform method employed in this study has enabled us to obtain two orders of magnitude improvement in the $B$-rotational constant.

The centrifugal distortion parameter $D_J$ is approximately half of the previously reported value (*7*). The difference can be attributed to the ability to resolve the $K$ components in the current study where as they were not resolved in the previous

TABLE I

Measured and Calculated $J + 1 \leftarrow J$ Transition Frequencies for Cyclobutadiene Iron Tricarbonyl

| $J$ | $K$ | Measured(MHz) | Calculated(MHz) | M-C(MHz) |
|---|---|---|---|---|
| 2 | 0 | 5771.893 | 5771.896 | -0.004 |
| 2 | 1 | 5771.893 | 5771.889 | 0.004 |
| 2 | 2 | 5771.865 | 5771.867 | 0.002 |
| 3 | 0 | 7695.843 | 7695.841 | 0.002 |
| 3 | 1 | 7695.843 | 7695.831 | 0.012 |
| 3 | 2 | 7695.793 | 7695.802 | -0.009 |
| 3 | 3 | 7695.759 | 7695.754 | 0.005 |
| 4 | 0 | 9619.761 | 9619.768 | -0.006 |
| 4 | 1 | 9619.761 | 9619.756 | 0.006 |
| 4 | 2 | 9619.717 | 9619.719 | 0.002 |
| 5 | 0 | 11543.668 | 11543.672 | -0.004 |
| 5 | 1 | 11543.668 | 11543.657 | 0.013 |
| 5 | 2 | 11543.601 | 11543.614 | -0.013 |
| 5 | 3 | 11543.547 | 11543.541 | 0.006 |
| 6 | 0 | 13467.545 | 13467.549 | -0.004 |
| 6 | 4 | 13467.272 | 13467.278 | -0.006 |
| 7 | 0 | 15391.408 | 15391.395 | 0.012 |
| 7 | 2 | 15391.303 | 15391.318 | -0.015 |
| 7 | 3 | 15391.224 | 15391.222 | 0.003 |
| 7 | 4 | 15391.093 | 15391.086 | -0.003 |

*Note.* Fit results using Eq. (1) with the present assignments are shown below with best fit parameter values given in Table II.

study. The previously measured transitions were broadened by 20 to 60 MHz half width, thus skewing the actual line center measurements due to the unresolved $K$ components.

$D_J$ can be used as a measure of how strongly the Cb-ring is bound to the Fe(CO)$_3$ group. To a crude approximation, CbFe(CO)$_3$ can be modeled as a psuedodiatomic where the Cb-ring and Fe(CO)$_3$ groups are regarded as point masses. Since $D_J$ is then

TABLE II

Best Fit Values for Adjustable Parameters Obtained Using Eq. (1) and Data in Table I

| parameter | present work | previous work |
|---|---|---|
| $B$ | 961.9856(8) MHz | 962.41 MHz |
| $D_J$ | 0.184(8) kHz | 0.41 kHz |
| $D_{JK}$ | 1.20(3) kHz | -- |

*Note.* The quoted errors are $2\sigma$ for the parameters and the $\sigma_{\text{FIT}} = 7.6$ kHz. Also shown are the results obtained from previous work (*7*).

TABLE III

Comparison of Distortion Parameters for Some Other Transition Metal Complexes with Values for CbFe(CO)$_3$

| Molecule | Distortion parameter | |
|---|---|---|
| | $D_J$(kHz) | $D_{JK}$(kHz) |
| CbFe(CO)$_3$ | 0.184(8) | 1.20(3) |
| Co(CO)$_3$NO | 0.17(8)[a] | 0.6 |
| CpNiNO | 0.08(2)[b] | 2.70(6) |
| CpMn(CO)$_3$ | 0.088(9)[c] | -0.04(3) |
| | $\Delta_J$(kHz) | $\Delta_{JK}$(kHz) |
| BuFe(CO)$_3$[d] | 0.075(2) | 0.16(1) |

[a] See Ref. (*14*).

[b] See Ref. (*13*).

[c] See Ref. (*10*).

[d] See Ref. (*15*). BuFe(CO)$_3$ = butadiene irontricarbonyl. $\Delta_J$ and $\Delta_{JK}$ smilar to the symmetric top $D_J$ and $D_{JK}$.

a measure of the susceptability to centrifugal distortion along this internuclear axis, the previous value of $D_J$ (see Table II) would indicate a more weakly bound complex than the current measurements indicate. The distortion parameters observed for CbFe(CO)$_3$ and other transition metal complexes (*3, 13–15*) are summarized in Table III. Unfortunately, there are no X-ray data for CbFe(CO)$_3$ to compare with the current microwave results. Older gas-phase electron diffraction studies (*5, 6*) provide some structure information and comparisons with our results are shown in Table IV.

There has previously been uncertainty whether the Cb-ring is square or slightly rectangular when complexed (*6*). The present results indicate that the Cb-ring is very nearly square when complexed to Fe(CO)$_3$. A rectangular structure would make $I_b$ and $I_c$ different thus producing an asymmetric-top spectrum. By modifying the electron diffraction coordinates (*5*) for the Cb-ring and assuming no change in the Fe(CO)$_3$ group, one can calculate the effects of a slightly rectangular structure for the Cb-ring. By making a 1-mÅ difference in the lengths of the two adjacent C–C bonds of the Cb ring, $B - C = 80$ kHz, and results in an asymmetry splitting in the spectrum of 230 kHz for the $J = 3 \leftarrow 2$ transition. The observed splitting is 30 kHz for this transition and is due to the small $D_{JK}$ value. Therefore, the vibrationally averaged structure of the Cb-ring appears to be square to better than 1 mÅ. Other structural anamolies in CbFe(CO)$_3$ can also be tested such as tilting the cyclobutadiene ring relative to the *a*-inertial axis. By calculating the effect of tilting the Cb-ring by ±2°, we can place an

TABLE IV

Rotational Constants of CbFe(CO)$_3$ Calculated from Electron Diffraction Studies and the Value Obtained from the Present Work

| | Present Work | Reference 6 | Reference 5 |
|---|---|---|---|
| $B$(MHz) | 961.9856(8) | 934.70 | 969.85 |

estimated value of $B - C = \pm 60$ kHz which would correspond to a 100-kHz asymmetry splitting in the spectrum. Therefore, we conclude that the Cb ring is vibrationally averaged to within less than ±2° of being perpendicular to the *a*-axis of the molecule. The overall structure of CbFe(CO)$_3$ is shown in Fig. 1; the $C_4$ axis of the cyclobutadiene ring and the $C_3$ axis of the Fe(CO)$_3$ are coincident with the *a*-molecular axis. The *b*- and *c*-axes are perpendicular to the *a*-axis, making $I_b$ and $I_c$ equal. This symmetrical structure is consistent with the observed spectrum.

The eclipsing of one of the corners of the Cb-ring with a carbonyl group and locking it into a fixed position would be detected only if the Cb-ring was tilted by this interaction. However, if a rigid, nontilted, eclipsed structure were present in CbFe(CO)$_3$, the moments of inertia would be the same as those observed in the present study. Therefore, a structure like this would still be consistent with the observed spectrum.

Finally, the possibility of hindered internal rotation of the cyclobutadiene ring relative to the Fe(CO)$_3$ group cannot be ruled out. Hindered rotation effects in symmetric tops are not observed (*16*), since the energy levels in a symmetric top are perturbed by hindered rotation equally in each rotational state, thus producing no observable splittings in the spectrum. Splittings could be produced by asymmetric isotopic substitution and this might reveal whether or not CbFe(CO)$_3$ undergoes internal rotation.

## CONCLUSION

Cyclobutadieneiron tricarbonyl is shown to be a symmetric-top molecule from the analysis of its high-resolution microwave spectrum. Evidence has been given to indicate that the Cb-ring has a square geometry in CbFe(CO)$_3$. A nontilting eclipsed structure cannot be distinguished from a staggered structure since the respective moments of inertia are identical and consistent with the observed spectrum. Hindered internal

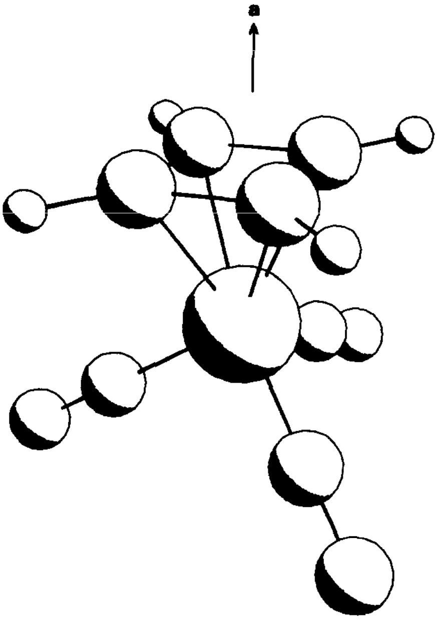

FIG. 1. Structure of CbFe(CO)$_3$. Coordinates obtained from Ref. (*5*). The *a*-inertial axis is colinear with the $C_4$ and $C_3$ axes of the cyclobutadiene and Fe(CO)$_3$, respectively.

rotation effects were not observed, however, evidence for such internal motion should be revealed by future isotopic studies.

## ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are grateful to the University of Arizona, Materials Characterization Program, for partial support of this research. The National Science Foundation provided funds for the construction of the PB-FTS. We thank Jon Wolgemuth for help in structural analysis and Professor Giles Henderson for stimulating conversations concerning cyclobutadieneiron tricarbonyl.

RECEIVED: January 31, 1992

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