

## Microwave Spectroscopy Measurements of Rotational Spectra and DFT Calculations for Two Distinct Structural Isomers of 1,1'-Dimethylferrocene

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**Abstract:** Microwave spectra were obtained for two distinct structural isomers of 1,1'-dimethylferrocene, an eclipsed synperiplanar isomer ( $\varphi = 0^\circ$ , the E0 isomer), with  $A = 1176.9003(2)$  MHz,  $B = 898.3343(2)$  MHz,  $C = 668.7469(2)$  MHz, and an eclipsed synclinal isomer ( $\varphi = 72^\circ$ , the E72 isomer) with  $A = 1208.7117(14)$  MHz,  $B = 806.4101(12)$  MHz, and  $C = 718.7179(8)$  MHz. The b-dipole, asymmetric-top spectra of both structural isomers were measured in the frequency range of 5–12 GHz using a Flygare–Balle type of spectrometer. A very good fit to observed transitions, with small distortion constants, was obtained for the E0 conformer, indicating that this conformer is nearly rigid. The deviations obtained in a similar least-squares fit for the E72 conformer are significantly larger, indicating possible fluxional behavior for this conformer. In addition, 7 out of the 26 transitions observed for the E72 isomer conformer clearly exhibit very small splittings, giving further evidence for internal motion. DFT calculations for the different possible conformations of 1,1'-dimethylferrocene arising from rotation of one methyl cyclopentadienyl ligand relative to the other about the nominal  $C_5$  axis by an angle  $\varphi$  (dihedral angle) were performed using the B3PW91 functional. The calculations converged and were optimized for five structures on this torsional potential energy surface corresponding to different dihedral angles  $\varphi$ ; three yielded energy minima, and two gave energy maxima, corresponding to transition states. The experimental results are in very good agreement with the results of the DFT calculations.

### Introduction

The characterization of ferrocene as a  $\pi$ -bonded complex by Wilkinson,<sup>1</sup> 50 years ago, played a central role in the development of organometallic chemistry. The solid-state structures of ferrocene and many ferrocene derivatives have been obtained using X-ray and neutron diffraction methods. However, the monosubstituted derivatives are often difficult to crystallize, and for the 1,1'-disubstituted derivatives, only one structural isomer has been observed in previous solid-state measurements. In the gas phase, monosubstituted derivatives are readily studied,<sup>2–4</sup> and multiple conformations of complexes have been observed.<sup>5</sup>

Disubstituted and monosubstituted ferrocenyl complexes are important precursors for the synthesis of many polyferrocenyl derivatives. These derivatives are polymers which may contain long hydrocarbon chains, nonfunctional spacers, or reactive organic functional groups and can have interesting and useful electronic and structural properties.<sup>6–9</sup> Examples, which have

recently been used for applications in materials science,<sup>10,11</sup> are polyferrocenylsilane and polymers with ferrocenedicarboxylate ligands. The derivatives of monosubstituted ferrocenyl complexes can be coupled to organic functional groups to generate a network of organic–inorganic polymers. Examples of these are a tetrakis(ferrocenyl)–nickel dithiolene complex and ferrocenyl dendrimers which possess multiple redox centers and could function as potential biosensors.<sup>12–14</sup> Another ferrocenyl derivative, *N,N*-dimethyl-1-ferrocenylethylamine, has been explored as a ligand for catalytic asymmetric reactions.<sup>15</sup> The ferrocenyl derivatives, such as polyferrocenylsilane, are possible building blocks for creation of materials with interesting semiconducting, magnetic, and optical properties.<sup>16–18</sup> The

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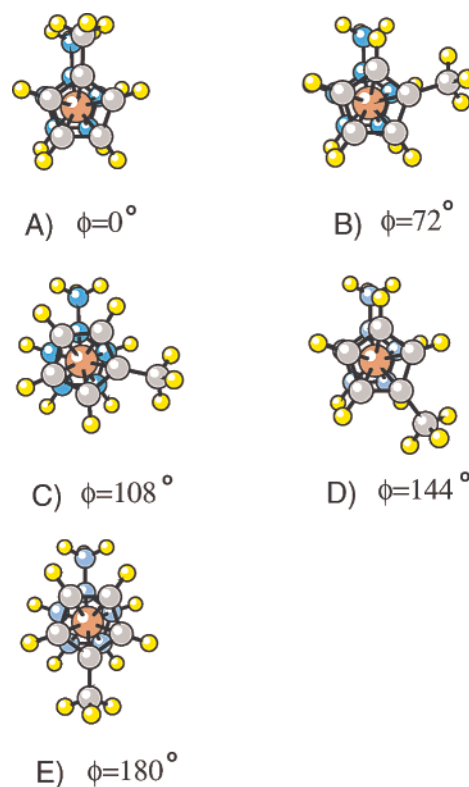
formation of these highly functionalized complexes, especially those that incorporate disubstituted ferrocenyl ligands, is dependent on the reactivity of the coordination site, conformational behavior, and possible steric hindrance. Steric interactions, in particular, play a significant role in determining the final structures and, therefore, can determine the chemical reactivity of the resulting complexes.

Dimethylferrocene is one of the few simple examples of a disubstituted ferrocenyl complex that can serve as a useful model for understanding the energetics and conformational dynamics associated with steric interactions in these complexes. There was no previous experimental data on the gas phase structure of dimethylferrocene and its various conformers, and only one conformer could be observed in the solid state.<sup>19</sup> It is hoped that the details of the structure and conformational behavior of dimethylferrocene can serve as a useful model to better understand the chemical, steric, and conformational behavior of a wide variety of more complex disubstituted ferrocenyl compounds.

The crystal structure of 1,1'-dimethylferrocene has been determined experimentally from X-ray work. For this solid-state structure, the eclipsed, synperiplanar conformation (E0 isomer,  $\varphi = 0^\circ$ ) is preferred, where the carbon atoms for the two  $C_5H_5$  rings are eclipsed and the methyl groups are cis relative to each other. No other structural conformers have been reported for the solid phase of dimethylferrocene, and none were previously observed for the gas phase.

The theoretical calculations for the torsional potential energy surface of dimethylferrocene, which are presented in this work, include five converged optimized structural conformations. A view down the  $z$ -axis (nominal symmetry axis of unsubstituted ferrocene) of each of the conformers considered is shown in Figure 1.

The labeling of the conformations follows the conventions given by Dong, Chun-ying, and Qing-jin.<sup>11</sup> Energies were calculated as a function of the relative orientation angle  $\varphi$ , the relative dihedral angle of the two methyl groups on the cyclopentadienyl ligands. The relative orientations of the methyl cyclopentadienyl ligands were initially fixed at  $0^\circ$  and the first five multiples of  $36^\circ$ . Converged structures were obtained for five of these angles, three corresponding to minimum-energy conformers and two which turned out to be transition states. For these calculations, all structural parameters were adjusted to obtain the fully optimized structures. Another theoretical study of torsional barriers on a similar type of diferrocenyl complex, 1,1'-di-*tert*-butylferrocene, indicated that the heights of the torsional barriers are very sensitive to the substituent groups.<sup>20,21</sup> The addition of bulky substituent groups tends to raise the torsional energy barrier of the complex, sometimes restricting it to only one energetically favorable conformer. For the dimethylferrocene complex, which has less sterically hindering substituents, several different conformers could exist in the gas phase, with similar populations.



**Figure 1.** This figure shows a view down the  $z$ -axis (nominal symmetry axis of unsubstituted ferrocene) for five distinct structural isomers of 1,1'-dimethylferrocene: (A) eclipsed synperiplanar isomer ( $\varphi = 0^\circ$ , the E0 isomer), (B) eclipsed synclinal isomer ( $\varphi = 72^\circ$ , the E72 isomer), (C) staggered anticlinal ( $\varphi = 108^\circ$ , the S108 isomer), (D) eclipsed anticlinal isomer ( $\varphi = 144^\circ$ , the E144 isomer), and (E) the staggered antiperiplanar isomer ( $\varphi = 180^\circ$ , the S180 isomer).

In this work, we report results of the first gas-phase measurements on two distinct structural isomers of 1,1'-dimethylferrocene, the eclipsed synperiplanar isomer ( $\varphi = 0^\circ$ , the E0 isomer) and an eclipsed synclinal isomer ( $\varphi = 72^\circ$ , the E72 isomer). This research is part of a larger program to understand the relation between structure and reactivity of transition metal complexes. Our previous microwave studies of some mono-substituted ferrocenyl derivatives, bromoferrocene,<sup>2</sup> chloroferrocene,<sup>3</sup> and methylferrocene,<sup>4</sup> clearly showed that the  $\eta_5 C_5H_5-Fe$ , carbon-iron bond distance is more sensitive to substitution on the cyclopentadienyl ligand than the C-C bond distances of the  $C_5H_5$  ring. From the previous microwave studies on these ferrocenes and other X-ray diffraction studies, we were able to infer that the single substitution of a halogen (Cl) had nearly the same influence on the  $\eta_5 C_5H_5-Fe$ , carbon-iron bond distance as the substitution of the two  $CH_3$  groups. In the present work, we now look, in more detail, at the effect of two  $CH_3$  substitutions and the lowest energy conformers associated with the relative orientations of the methylcyclopentadienyl ligands. This work has yielded new information on the torsional behavior of the dimethylferrocene complex. The analyses of rotational spectra of the two observed structural isomers have shown that the E0 isomer ( $\varphi = 0^\circ$ ) is more nearly a rigid rotor, compared with the E72 isomer ( $\varphi = 72^\circ$ ). Several transitions of the E72 isomer clearly exhibit small splittings that were not observed for the E0 isomer. This suggests fluxional behavior associated with this E72 conformer.

An important part of this analysis of the conformational dynamics and structure of dimethylferrocene is the comparison

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of the experimental results with theoretical calculations and previous data from microwave experiments on the monosubstituted ferrocenyl derivatives. Although the calculations have yielded five converged structures (E0, E72, E144, S108, S180), three of which presumably could exist in the gas phase for 1,1'-dimethylferrocene, only the two conformers, E0 and E72, were detected in this work.

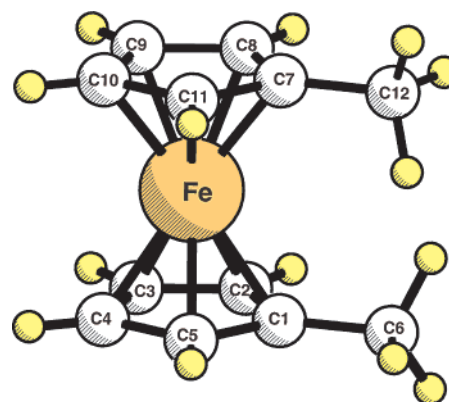
### Experimental Methods and Results

A sample of 90% purity 1,1'-dimethylferrocene was purchased from Strem Chemicals. This sample was resublimed to further improve the purity before use in the spectrometer. Because dimethylferrocene is an air-sensitive complex, all sample manipulation was done under an oxygen free environment. The sample was resublimed at 0.1 Torr of pressure, between 37 and 40 °C. This solid, orange-yellow resublimed sample was transferred into a glass cell for the measurements. During the run, the sample cell and General Valve, Series-9 pulsed valve was heated to 33–35 °C in order to produce sufficient vapor pressure from the solid sample. The sample was seeded in neon carrier gas at 0.7 atm pressure and pulsed into the vacuum chamber. The optimal backing pressure of the neon gas was 0.7–0.8 atm, and this was maintained throughout the experiment. The observed signal-to-noise ratio depends on many factors, such as cavity mode, cavity Q, and the various time delays, which were adjusted to optimize the signal-to-noise ratio. The sample was pulsed into the microwave cavity at a constant pulse rate, typically 2 Hz, and frequency scans were done in the 4–12 GHz frequency range. The spectrometer used for this work is a Flygare–Balle type pulse beam microwave spectrometer developed in this laboratory.<sup>22</sup> The typical line width obtained with this instrument is about 20 kHz, in the 10 GHz range, with neon carrier gas.

Rotational spectra were measured in the 5–12 GHz range. The observed transitions could be assigned to b-dipole, asymmetric-top transitions for either the E0 or E72 conformer. Over 50 R-branch rotational transitions were obtained for the normal, <sup>56</sup>Fe isotopomers. The transitions observed for the lower J and K states are quite strong due to the rotational cooling in the supersonic jet expansion. For some of the lower-J transitions, a free induction decay signal was observed for the normal isotopomer with a 5:1 S/N ratio with a single beam pulse. The molecular signal from the cavity was passed through a liquid-nitrogen cooled, MITEQ low-noise amplifier. This amplifier significantly improved the spectrometer S/N ratio and greatly facilitated detection of the low abundance isotopic species. The observed transitions for the single-<sup>13</sup>C and other low-abundance isotopomers typically required over 1000 shots of signal averaging. The rotational transitions for <sup>54</sup>Fe (both isomers) and one of the <sup>13</sup>C isotopomers of the E0 conformer were obtained in the natural abundance sample. No <sup>13</sup>C isotopomer transitions were obtained for the E72 conformer. Many search attempts were done to observe other unique <sup>13</sup>C isotopomers but were only partially successful. Only four transitions for <sup>13</sup>C at the C<sub>2</sub> position were obtained for the E0 conformer. The basic structure of the complex and atom numbering scheme is shown in Figure 2.

Two transitions were obtained for <sup>13</sup>C at the C<sub>3</sub> position for the E0 conformer, but unfortunately this was not enough data to give reliable fits. For the <sup>54</sup>Fe isotopomers, eight transitions were obtained for the E0 conformer and seven transitions for the E72 conformer, all of which could be reasonably well fit using the three rotational constants as variable parameters, with distortion constants fixed at normal isotopomer values.

Extensive searches, within ±100 MHz of the predicted frequencies, were carried out for two other distinct isomers, E144 and S108. Predictions of the frequencies for all polar isomers were generated using coordinates produced from DFT calculations, which proved to be accurate to within about two ±2.0% or better (see computational and



**Figure 2.** Structure of the eclipsed, synperiplanar (E0) conformer of 1,1'-dimethylferrocene, indicating the numbering scheme for the carbon atoms.

discussion sections). However, no transitions were observed for the E144 and S108 isomers.

### Data Analysis and Results

The asymmetric-top rotational spectra of 1,1'-dimethylferrocene, observed in the frequency range of 5–12 GHz, were analyzed using a least-squares fitting procedure. The observed rotational transitions are R-branch b-dipole type transitions. The experimental “stick plot” spectra were generated, by plotting all measured frequencies using the measured relative intensities. This appeared to be a fairly complex spectrum due to the presence of the two different structural isomers, small asymmetry splittings, and possible methyl torsional motion. The observed “stick plot” transitions were then assigned quantum numbers by comparing them with plots of the theoretical spectra. Theoretical spectral plots were generated for b-dipole transitions for three structural isomers: the E0 conformer, the E72 conformer, and the eclipsed anticlinical (E144) conformer, with  $\varphi = 144^\circ$ . The conformer with  $\varphi = 180^\circ$  is the staggered antiperiplanar conformer and is a transition state structure with the highest calculated energy and a zero dipole moment, so it would not be observed in these experiments (see the computational section below). Three calculated parameters, the A, B, and C rotational constants, were used to generate theoretical spectra, with the centrifugal distortion constants assumed to be zero at this stage of analysis. The theoretical rotational constants for the three isomers were obtained from DFT calculations as discussed below. The spectrum of the E0 conformer was also generated using the rotational constants obtained from the X-ray diffraction structure. By carefully comparing the simulated theoretical spectrum with the experimental “stick plot” spectrum, we were able to recognize that many of the observed transitions were due to only two structural isomers, the E0 isomer ( $\varphi = 0^\circ$ ) and the E72 isomer ( $\varphi = 72^\circ$ ). Using this procedure, we were able to assign rotational quantum numbers for one or the other of these two isomers to the most observed transitions in the “stick plot” spectrum. The accuracy of the assignments was verified by carrying out least-squares fits with the Pickett fitting program (SPFIT).<sup>23</sup> The observed transitions were fit using Watson’s A-reduced Hamiltonian with three rotational constants and quartic distortion terms. For the E0 isomer, only four spectroscopic parameters were needed to obtain an excellent

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**Table 1.** Molecular Parameters Obtained from SPFIT Fits for 1,1'-Dimethylferrocene (E0) and 1,1'-Dimethylferrocene (E72) Isotopomers  $^{56}\text{Fe}$ ,  $^{54}\text{Fe}$ , and  $^{13}\text{C}_2^a$ 

parameter	E0 $^{56}\text{Fe}$	E0 $^{54}\text{Fe}$	E0 $^{13}\text{C}_2$	E72 $^{56}\text{Fe}$	E72 $^{54}\text{Fe}$
<i>A</i>	1176.9003(2)	1177.6260(6)	1173.3239(7)	1208.7117(14)	1209.2730(9)
<i>B</i>	898.3343(2)	898.3088(4)	891.9184(4)	806.4101(12)	806.3861(15)
<i>C</i>	668.7469(2)	668.9662(4)	666.3343(4)	718.7179(8)	718.8974(3)
$\Delta_J$	0.000 0175(20)	0.000 017 5 <sup>b</sup>	0.000 017 5 <sup>b</sup>	0.000 128(20)	0.000 128 <sup>b</sup>
$\Delta_{JK}$				-0.000 320(83)	-0.000 320 <sup>b</sup>
$\Delta_K$				0.000 279(73)	0.000 279 <sup>b</sup>
$\delta_J$				0.000 069(10)	0.000 069 <sup>b</sup>
$\sigma(\text{fit})$	2.9	3.9	1.9	5.9	5.1

<sup>a</sup> The frequency and listed errors ( $1\sigma$ ) are reported in MHz. The standard deviations of the overall fit,  $\sigma(\text{fit})$ , are in kHz. <sup>b</sup> Fixed parameter.

fit of the transitions, with low residuals. The variable parameters used are the three rotational constants, *A*, *B*, and *C*, and one quartic distortion constant,  $\Delta_J$ . The attempts to fit rotational transitions for the E72 isomer required additional quartic distortion terms in order to obtain reasonably good fits. The seven parameters *A*, *B*, *C*,  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ , and  $\delta_J$  were used in fitting the transitions for the 1,1'-dimethylferrocene E72 isomer. The molecular parameters obtained from the spectral fits for the E0 isomer and the E72 isomer are given in Table 1. The measured transition frequencies are available as Supporting Information (Table S1). 10 observed lines could not be successfully assigned at this stage of analysis.

The measured rotational constants obtained from the least-squares fits for the E0 isomer and the E72 isomer were used to predict rotational constants of  $^{54}\text{Fe}$  and  $^{13}\text{C}$  isotopomers. Coordinates from the theoretical structure were used to obtain calculated ratios of the rotational constants for the  $^{54}\text{Fe}$  and  $^{13}\text{C}$  isotopomers to rotational constants for the normal isotopomers. These ratios were used to scale the observed rotational constants in order to predict rotational spectra of  $^{54}\text{Fe}$  and  $^{13}\text{C}$  isotopic species. The frequency predictions for the  $^{54}\text{Fe}$  and  $^{13}\text{C}$  isotopomers obtained using this method turned out to be very accurate. The measured transitions for the  $^{54}\text{Fe}$  and  $^{13}\text{C}$  isotopic species were observed within  $\pm 1.0$  MHz of the predicted transitions. The high accuracy of these isotopic frequency predictions for the two  $^{54}\text{Fe}$  isotopic species provided considerable confidence in the original assignments of the strong, normal isotopomer lines to the two different structural isomers. Following these assignments, some of the observed transitions that were not previously assigned could now be assigned to the  $^{54}\text{Fe}$  isotopomers. The observed rotational transitions for the  $^{54}\text{Fe}$  and  $^{13}\text{C}$  isotopic species were fit using only three variable parameters, the *A*, *B*, and *C* rotational constants. The centrifugal distortion constants were fixed to the values obtained for the corresponding normal, parent species. The parameters obtained for  $^{54}\text{Fe}$  and one of the  $^{13}\text{C}$  isotopic species are shown in Table 1. The corresponding measured transition frequencies are given as Supporting Information (Tables S2, S3, and S5).

Since a least-squares fit to the observed rotational transitions for the E0 isomer was obtained using only four parameters, with a standard fit deviation of only  $\sigma_{\text{fit}} = 2.9$  kHz, it appears that the structure of the E0 isomer is nearly rigid. The three rotational constants, *A*, *B*, *C*, and one quartic centrifugal distortion constant,  $\Delta_J$ , are given in Table 1. The listed error limits are  $1\sigma$ . The  $\Delta_J$  value is very small (0.0175(20) kHz) and provides further evidence for a rigid structure.

Seven spectroscopic parameters were determined from the least-squares fit of observed transitions for the E72 isomer. In addition to the three rotational constants, *A*, *B*, *C*, and four

quartic centrifugal distortion constants,  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$ , were also determined. The  $\Delta_J$  value obtained for the E72 isomer of 1,1'-dimethylferrocene is about 0.1 kHz, a factor of 6 larger than the  $\Delta_J$  value for the E0 isomer of 1,1'-dimethylferrocene. The  $\Delta_{JK}$  and  $\Delta_K$  values are nearly three times the value of  $\Delta_J$ . Although, these distortion constants are small relative to the rotational constants, they provide an indication of a less rigid structure. The standard deviation of the fit for the E72 isomer is  $\sigma(\text{fit}) = 5.9$  kHz, about 2 times larger than the standard deviation obtained for the E0 isomer. This standard deviation of 5.9 kHz still indicates a rather good fit, considering the additional line splittings observed for this isomer. We observed seven transitions for the E72 isomer that clearly exhibited line splittings that were not observed for the E0 isomer. These splittings are quite small, about 0.04–0.3 MHz in magnitude, and were observed only for the E72 isomer. We believe that these splittings are most likely due to torsional motion of the methyl groups. For an asymmetric top molecule that possesses two independent methyl torsional rotors, the analysis and fitting of line splittings due to the coupling between overall rotation and two independent methyl torsional motions could be very challenging. However, because these observed splittings are small, we could select only the frequency that appeared to best represent the center frequency and use these frequencies in the fit. Including these “line centers” in the fit yielded about the same standard deviation as the “test” fit that excluded them. These results provide further indication that the E72 conformer behaves somewhat differently than the E0 conformer.

### Structural Analysis

The amount of available isotopomer data was rather limited for such a large molecule so the structural fit for the E0 isomer was done with only a few variable structural parameters. For the E72 isomer, no  $^{13}\text{C}$  isotopomers were obtained, so a structural fit could not be done. Calculated structural parameters for the E72 isomer are given in the Supporting Information, Table S9. Many of the structural parameters were fixed at values obtained from the DFT calculations. The basic structure of the 1,1'-dimethylferrocene complex, with the numbering scheme used for the carbon atoms, is shown in Figure 2. The two structural parameters selected as variable parameters in the fit to determine the structure are the distance from the Fe atom to the center of the  $\text{C}_5$  ring ( $R_{\text{Fe}-\text{Cp}}$  or  $P_1$ ) and the radius of the  $\text{C}_5$  ring ( $R_{\text{Cp}}$  or  $P_2$ ). A total of 9 rotational constants obtained from the least-squares fits for the  $^{56}\text{Fe}$ ,  $^{54}\text{Fe}$ , and  $^{13}\text{C}$  observed transitions were used in the structural fit. The initial structure used in the structural fit program had the top and bottom cyclopentadienyl (Cp) rings eclipsed and all five carbon atoms of each Cp rings located in the respective *xy* planes perpen-

**Table 2.** Results of Structural Fits for 1,1'-Dimethylferrocene (E0) with Two Variable Parameters ( $P_1 = \text{Cp-Fe Centroid Distance}$ ,  $R_{\text{Cp-Fe}}$ , and  $P_2 = \text{Cp Radius}$ ,  $R_{\text{Cp}}$ )<sup>a</sup>

parameter	measured	fit I calculated	fit II calculated	fit III calculated
$A(^{56}\text{Fe})$	1176.9003	1177.4587	1177.6061	1177.6068
$B(^{56}\text{Fe})$	898.3343	897.4096	897.9173	897.8938
$C(^{56}\text{Fe})$	668.7469	670.1804	669.1951	668.1821
$A(^{54}\text{Fe})$	1177.6260	1178.5887	1178.6477	1178.6484
$B(^{54}\text{Fe})$	898.3088	897.4096	897.9173	897.8938
$C(^{54}\text{Fe})$	668.9662	670.5463	669.5313	669.5183
$A(^{13}\text{C}_2)$	1173.3239	1171.5252	1171.5921	1171.5907
$B(^{13}\text{C}_2)$	891.9184	892.1322	892.7478	892.7952
$C(^{13}\text{C}_2)$	666.3343	666.2084	665.2861	665.3121
$P_1 = R_{\text{Cp-Fe}}$		1.670(7)	1.684(6)	1.670(6)
$P_2 = R_{\text{Cp}}$		1.220(5)	1.224(4)	1.224(4)
$\sigma(\text{fit})$		1.2	1.0	1.0

<sup>a</sup> For fit I, the  $R_{\text{Fe-Cp}}$  centroid distance and the Cp ring radius are allowed to vary. For fit II, small corrections are added to  $\eta_5$  Fe-C bond distances with 0° tilting of the methyl groups. For fit III, small corrections added to  $\eta_5$  Fe-C bond distances with 2.66° tilting of methyl groups. The frequency and fit deviation ( $\sigma(\text{fit})$ ) are reported in MHz.  $P_1$  and  $P_2$  are in angstrom, and listed are  $1\sigma$ .

dicular to the Fe-Cp axis. This constraint makes all of the  $\eta_5$  Fe-C bond distances equal for the top and bottom Cp rings. The carbon atoms of the CH<sub>3</sub> groups attached to the top and bottom Cp rings were also constrained to lie in the same  $xy$  plane as Cp carbon atoms and, for the E0 isomer, are cis relative to each other ( $\varphi = 0^\circ$ ). For fit I, shown in Table 2, the Fe-Cp centroid distance ( $R_{\text{Fe-Cp}}$ ) and the Cp ring radius ( $R_{\text{Cp}}$ ) were allowed to vary. The structure fitting calculations converged within three iterations. For fit II, small corrections (based on the difference between the theoretical and experimental  $\eta_5$  Fe-C bond distances) were added to  $\eta_5$  Fe-C bond distances. These “corrections” were made for all 10  $\eta_5$  Fe-C bond distances. A 0° tilt angle (which places the methyl C atom in the same plane as the Cp C atoms) was used for both methyl groups for fits I and II. For fit III, these same small corrections were added to the  $\eta_5$  Fe-C bonding distance along with a 2.66° tilt angle of the methyl groups away from  $xy$  planes (defined by the Cp ring), for both methyl groups. The value for the tilt angle of 2.66° was obtained from previous microwave studies of methylferrocene,<sup>4</sup> and a similar value (3.2°) was obtained for the DFT calculated structure (see Table S8, Supporting Information) and previous measurements on chloroferrocene.<sup>3</sup> The results of these structural fits for the E0 conformer are shown in Tables 2 and 3. Although the standard deviations for fits I–III are very similar, we believe that fit III gives a more accurate representation of the structure, because the proper tilt angle has been included.

## Computational Methods and Results

We also wish to report results of a theoretical study of dimethylferrocene conformations, carried out using the density functional theory method (DFT).<sup>24–26</sup> The calculations were performed exclusively using the B3PW91 hybrid functional of Beck, Perdew, and Wang. From our previous experience with gas-phase structures using B3PW91,<sup>25</sup> rotational constants for most of the transition metal complexes studied can be predicted quite accurately. This appears to be true for the present DFT calculations also.

**Table 3.** Comparison of the Bond Lengths for the DFT Calculation and Results of Fits I–III for 1,1'-Dimethylferrocene (E0)<sup>a</sup>

parameter	DFT	fit I	fit II	fit III
C <sub>1</sub> –C <sub>2</sub>	1.432	1.435(3)	1.437(2)	1.437(2)
C <sub>2</sub> –C <sub>3</sub>	1.428	1.435(3)	1.432(2)	1.432(2)
C <sub>3</sub> –C <sub>4</sub>	1.428	1.435(3)	1.432(2)	1.432(2)
C <sub>4</sub> –C <sub>5</sub>	1.428	1.435(3)	1.432(2)	1.432(2)
C <sub>5</sub> –C <sub>1</sub>	1.432	1.435(3)	1.437(2)	1.437(2)
Fe–C <sub>1</sub>	2.065	2.068(9)	2.079(8)	2.068(8)
Fe–C <sub>2</sub>	2.050	2.068(9)	2.064(8)	2.053(8)
Fe–C <sub>3</sub>	2.046	2.068(9)	2.060(8)	2.049(8)
Fe–C <sub>4</sub>	2.046	2.068(9)	2.060(8)	2.049(8)
Fe–C <sub>5</sub>	2.050	2.068(9)	2.064(8)	2.053(8)
$\angle\text{Fe-C}_7\text{-C}_{12}$	130.0	127.0 <sup>b</sup>	127.0 <sup>b</sup>	129.7 <sup>b</sup>
$\angle\text{Fe-C}_1\text{-C}_6$				
CH <sub>3</sub> TILT angle	3.2	0	0	2.66

<sup>a</sup> Note that hydrogen, C<sub>1</sub>–CH<sub>3</sub>, and C<sub>7</sub>–CH<sub>3</sub> bond lengths are fixed during the structural fit (All C–H(Cp) = 1.077 Å, C–H(CH<sub>3</sub>) = 1.088 Å, and C<sub>1</sub>–CH<sub>3</sub> = C<sub>7</sub>–CH<sub>3</sub> = 1.495 Å). Bond lengths are reported in angstrom, and angles are in degrees. The CH<sub>3</sub> TILT angle indicates the amount that the C–CH<sub>3</sub> bond is tilted out of the cyclopentadienyl plane in a direction away from the Fe atom. The listed errors for bond lengths are  $1\sigma$ . <sup>b</sup> Fixed parameter.

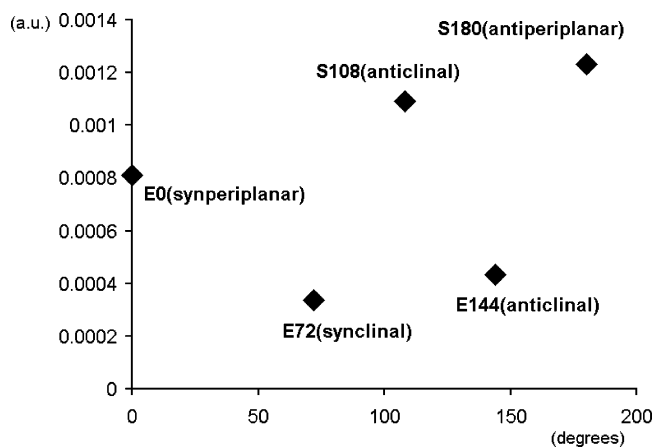
**Table 4.** Torsional Potential Energy and Total Dipole Moment for the Optimized Structures of Dimethylferrocene Obtained from DFT Calculations<sup>a</sup>

dihedral angle $\varphi$	conformation notation	energy (au)	relative energy (au)	total dipole (debye)
180	S180 (TS <sup>b</sup> )	–588.704 766 9	0.001 233 1	0.0035
144	E144	–588.705 567 5	0.000 432 5	0.1809
108	S108 (TS <sup>b</sup> )	–588.704 909 5	0.001 090 5	0.3556
72	E72	–588.705 663 8	0.000 336 2	0.4612
0	E0	–588.705 189 8	0.000 810 2	0.5672

<sup>a</sup> The calculations were performed with the B3PW91 using SVP basis sets for carbon and hydrogen and Hay Wadt ( $n + 1$ ) ECP VDZ basis sets for Fe. The energies are given relative to –588.706 au. <sup>b</sup> TS = transition state.

All density functional calculations were performed on an IBM-640 cluster computer (TINTIN) using the Gaussian 98 programs<sup>27</sup> at the University of Arizona. Large basis sets, including split-valence plus polarization (SVP<sup>28</sup> basis set), were selected for carbon and hydrogen. For the Fe basis set and effective core potential, we used the Hay and Wadt ( $n + 1$ ) ECP VDZ basis set.<sup>29</sup> Frequency analyses were done to check that the local energy minima obtained are stationary points. DFT calculations for the different possible conformations of 1,1'-dimethylferrocene arising from rotation of one methyl cyclopentadienyl ligand relative to the other about the nominal C<sub>5</sub> axis ( $z$ -axis), were performed for different values of this rotation angle  $\varphi$ . For most of the calculations, the two methyl groups were initially fixed relative to each other at various dihedral angles from  $\varphi = 0^\circ$  to  $180^\circ$ , and the remaining geometry was subsequently optimized using the Berny algorithm with redundant internal coordinates. The results are shown in Table 4 and Figure 3.

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**Figure 3.** Torsional potential energy as a function of internal torsional angle  $\varphi$  (dihedral angle) for the five optimized structural isomers of 1,1'-dimethylferrocene. These structures and the relative energies for the five conformers of dimethylferrocene were obtained from the B3PW91 calculations. The energies are given in au relative to  $-588.706$  au.

**Table 5.** Rotational Constants for Various Optimized 1,1'-Dimethylferrocene Conformers Obtained from DFT Calculations<sup>a</sup>

conformation notation	A (MHz)	B (MHz)	C (MHz)
DFT			
E0	1179.4144	890.5905	665.0750
E72	1217.2576	791.8683	713.9339
S108 (TS <sup>b</sup> )	1265.3724	740.5962	727.3466
E144	1354.0793	765.1434	665.3122
S180 (TS <sup>b</sup> )	1389.5982	722.3660	646.1935
Microwave			
E0	1176.9003(2)	898.3343(2)	668.7469(2)
E72	1208.7116(13)	806.4102(11)	718.7179(7)
X-ray <sup>c</sup>			
E0	1217.7705	910.1389	677.7796

<sup>a</sup> The calculations were performed with the B3PW91 using SVP basis sets for carbon and hydrogen and Hay Wadt ( $n + 1$ ) ECP VDZ basis sets for Fe. Experimental rotational constants are given for comparison. <sup>b</sup> TS = transition state. <sup>c</sup> Rotational constants calculated from the geometry (see ref 19).

Beginning with the various possible eclipsed and staggered conformations of the Cp carbon atoms, five dihedral angles were found, which led to converged structures, which are expected to be local minima on this torsional potential energy surface. Using these five conformations, all structural parameters were fully optimized, and these results are shown in Figure 3 and Table 4. The E0, E72, and E144 optimized structures for 1,1'-dimethylferrocene were obtained without imaginary frequencies: eclipsed synperiplanar ( $\varphi = 0^\circ$ , E0), eclipsed synclinal ( $\varphi = 72^\circ$ , E72), eclipsed anticlinal ( $\varphi = 144^\circ$ , E144). Two optimized structures for 1,1'-dimethylferrocene were obtained with imaginary frequencies: staggered anticlinal ( $\varphi = 108^\circ$ , S108) and staggered antiperiplanar ( $\varphi = 180^\circ$ , S180). Here, staggered denotes staggering of the five carbon atoms of the Cp rings, and eclipsed denotes eclipsed carbon atoms of the Cp rings. The rotational constants obtained from the DFT calculations for these five distinct structural isomers are given in Table 5, and the optimized coordinates are given as Supporting Information (see Table S8–S12). Other dihedral angles were chosen, at  $15^\circ$ ,  $52^\circ$ ,  $62^\circ$ ,  $82^\circ$ , on the torsional potential energy surface, and the corresponding structures were fully optimized. Structures fixed at these angles however did not meet the convergence criteria, and the one initially fixed at  $15^\circ$  collapsed to the eclipsed synperiplanar ( $\varphi = 0^\circ$ , E0) structure. Only two of the five calculated structural isomers were observed in these experiments on 1,1'-dimethylferrocene, the eclipsed synperiplanar ( $\varphi = 0^\circ$ , E0) and eclipsed anticlinal ( $\varphi = 72^\circ$ , E72)

conformations. The results of the calculations are given in Tables 3–5. In Table 3, the structural parameters for the E0 conformer obtained from the structural fit are compared with the DFT calculated results. The calculations also indicate that the  $C_5$  symmetry for the Cp groups is preserved to within a few thousandths of an angstrom, in support of the assumptions and constraints used for the structural fits.

## Discussion

Some of the key structural parameters for two distinct conformations of gas-phase 1,1'-dimethylferrocene have been determined from the high-resolution microwave measurements. To obtain these structural parameters, however, we rely heavily on results of the DFT calculations, since data for only a few of the unique  $^{13}\text{C}$  isotopomers were obtained. The fitted structural parameters, nevertheless, appear to be in good agreement with the theoretical structural parameters, and the combined experimental and theoretical results yield a consistent picture of the low energy conformations of this complex. The second one of the three possible stable conformers, the eclipsed anticlinal (E72) conformer, has been experimentally detected for the first time. The rotational constants for the E0 conformer, ( $A = 1176.9003(2)$ ,  $B = 898.3343(2)$ ,  $C = 668.7469(2)$  MHz) obtained from the fits are in excellent agreement (with deviations less than  $\pm 1\%$ ) with the calculated DFT values, as can be seen in Table 5. Rotational constants for the DFT-calculated structure of the E0 conformer of 1,1'-dimethylferrocene are  $A = 1179.414$ ,  $B = 890.591$ , and  $C = 665.075$  MHz. This excellent agreement strongly supports the identification of this conformer as the eclipsed synperiplanar (E0) conformation. The results of the least-squares structural fits further support this assignment (see Table 3). The experimental distortion constant,  $\Delta_J$ , is very small for this conformer (0.0175(20) kHz), indicating a fairly rigid structure. The calculated rotational constants from the solid-phase structure for 1,1'-dimethylferrocene are  $A = 1217.7705$ ,  $B = 910.1389$ ,  $C = 677.7796$  MHz (see Table 5). These values from the solid-phase structure are somewhat larger than the microwave and DFT values, showing some evidence for the possible effects of crystal packing forces.

The rotational constants for the second experimental conformer agree very well (with deviations less than  $\pm 2\%$ ), with the DFT calculated values for the eclipsed synclinal ( $\varphi = 72^\circ$ , E72) conformer, so this second experimental conformer is assigned to the E72 conformation of 1,1'-dimethylferrocene. From the seven-variable least-squares fit results, the observed rotational constants for the E72 conformer are  $A = 1208.7117(14)$ ,  $B = 806.4101(12)$ , and  $C = 718.7179(8)$  MHz. The quartic centrifugal distortion constants determined for this conformer are reasonably small ranging from 0.1 to 0.3 kHz. The small frequency splittings observed only for the E72 conformer are most likely due to torsional motion of the methyl group. It seems reasonable that this could result from the torsional barriers being lower for the E72 conformer than for the E0 conformer.

The following DFT theoretical rotational constants were obtained for the eclipsed synclinal ( $\varphi = 72^\circ$ ) conformer:  $A = 1217.2576$ ,  $B = 791.8683$ ,  $C = 713.9339$  MHz, and the theoretical rotational constants for the staggered anticlinal ( $\varphi = 108^\circ$ ) conformer are  $A = 1265.3724$ ,  $B = 740.3962$ ,  $C = 727.3466$  MHz. Since these calculated values for the staggered anticlinal ( $\varphi = 108^\circ$ ) isomer deviate by as much as  $\pm 9\%$  from the experimental values, whereas the E72 values are in agree-

ment, we believe that the second observed experimental conformer must be the eclipsed anticlinal (E72,  $\varphi = 108^\circ$ ) conformer.

The standard deviations for all three of the structural fits listed in Table 3 are very good, but if we compare the structures obtained from the fits with the structures from the DFT calculations, we see a further indication that fit III gives the preferred gas-phase structure for the E0 conformer of 1,1'-dimethylferrocene. It is important to recognize the fact that, without adding a tilt of the methyl-groups, relative to the Cp carbon plane, as is done for fit III, the  $\eta_5$  Fe-C bond distances from the fit would be significantly longer than the DFT values. So we believe that the  $\eta_5$  Fe-C bond distances obtained from fit I and fit II do not agree as well with the DFT-calculated values as those from fit III. The effects of this "tilt angle" suggest that a steric interaction between two methyl groups plays a significant role in determining the lowest energy structure. Interestingly, the  $2.66^\circ$  tilt appears to be a "normal" tilt angle for these types of ferrocenyl derivatives. We have observed very similar values of this tilt angle for methylferrocene,<sup>2</sup> chloroferrocene,<sup>3</sup> and bromoferrocene.<sup>4</sup>

The eclipsed anticlinal ( $\varphi = 144^\circ$ ) structure is calculated to be the second most stable conformer, as a function of  $\varphi$ , but this conformer was not detected in the present microwave work. This could be due, in part, to the relatively low dipole moment of 0.18 D. We also note that the staggered anticlinal ( $\varphi = 108^\circ$ , S108) also was not observed in the present microwave work. However, we note that the energy of this conformation (see Table 5 and Figure 3) is significantly higher than that of the E0 and E72 conformers, and the dipole moment is lower. In addition, the staggered anticlinal S108 isomer was predicted to exist as a transition state structure, which could move along the torsional potential energy surface toward a more energetically stable structure.

## Conclusions

The results of high-resolution microwave measurements provide useful, new information on the structures and conformational behavior of the 1,1'-dimethylferrocene complex. Two distinct structural isomers of dimethylferrocene were clearly

detected in the present study, and structural parameters for these two conformers were obtained. The more rigid observed isomer can be unambiguously assigned to the eclipsed synperiplanar (E0,  $\varphi = 0^\circ$ ) conformer of 1,1'-dimethylferrocene. The gas-phase structural parameters obtained from this experiment are in excellent agreement with present DFT calculations for this E0 conformer. Structural parameters for the second, less rigid conformer are in very good agreement with the DFT calculations for the eclipsed anticlinal (E72) conformer. The observed spectral lines for the E72 conformer clearly exhibited very small splittings. These small splittings could be due to hindered rotation effects of the methyl groups or hindered rotation of the Cp groups about their common axis. The torsional potential energy surface provided by present DFT calculations provides a very good picture of the relative energies for the different conformations of 1,1'-dimethylferrocene. Two of the three calculated lower energy conformations were observed and characterized. It would be desirable to have more extensive, high level calculations to obtain more accurate relative energies of the conformations and finer details of the torsional potential energy surface, but the present overall results from the experiments and calculations seem quite consistent. With a better torsional potential energy surface, the detailed dynamics of the torsional motion and "torsionally averaged" structures could be calculated and these structures may agree better with the experimental results.

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**Supporting Information Available:** Tables of measured frequencies and assignments for 1,1'-dimethylferrocene E0, 1,1'-dimethylferrocene E72 isomers, their isotopic derivatives, and calculated atomic coordinates. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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