MEASUREMENTS OF MICROWAVE SPECTRA AND STRUCTURAL PARAMETERS FOR METHYL FERROCENE[a]

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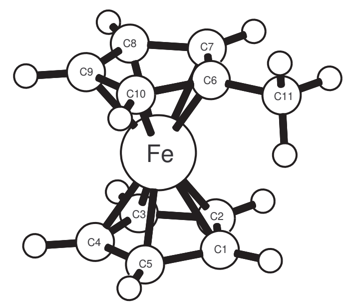
Rotational transitions in the 4-12 GHz range were measured using a Flygare-Balle type, pulsed-beam Fourier transform spectrometer. Mono-substituted ferrocenes are near-prolate asymmetric tops with a and b dipole moment components, providing numerous possible transitions in this frequency range. Eighteen rotational constants were calculated from the data for six isotopomers. 59 transitions were measured for the normal isotopomer, and much smaller data sets were obtained for the ^{54}Fe, and four ^{13}C isotopomers. Despite the small data sets for ^{13}C and ^{54}Fe, transitions, good fits were obtained with small standard deviations ranging from 2-5 KHz. The eighteen A, B, and C rotational constants were used to determine the final geometry of Methyferrocene. Measured rotational constants for the normal isotopomer are: A = 1592.6050 (6), B = 957.2565 (4), and C = 825.9892 (4) MHz. No evidence for internal rotation was observed in the spectra. The structure of this complex was calculated using DFT methods, and the results are in good agreement with the measurements. The changes in the structure caused by substitutions on the cyclopentadienyl ligand are compared with earlier results on chloroferrocene and bromoferrocene. For chloroferrocene, the C-Cl bond is bent 3° up from the plane of carbon atoms, and the substituted C_5H_4Cl ligand is tilted 1.4° with respect to the unsubstituted C_5H_5 ligand. Distortions of the substituted cyclopentadienyl ligand for methyl ferrocene are smaller than those observed for chloroferrocene.



[a]Supported by THE NATIONAL SCIENCE FOUNDATION