THE ROTATIONAL BARRIER IN METAL SANDWICH COMPOUNDS

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The vibrational spectra of metallocenes and dibenzene-metal complexes have been of considerable value in helping elucidate the bonding forces present in these molecules.[1-3] The skeletal vibrations, in particular, are useful for evaluating ring to metal forces.[4] The torsional frequency, however, cannot be observed directly under normal conditions for π–Cp_2M or $(\pi$–$C_6H_6)_2M$ compounds since the vibration is inactive in both infrared and Raman spectra. This is unfortunate since knowledge of this frequency would make it possible to directly evaluate the potential barrier to internal rotation in a di-ring molecule.

In this note the torsional frequencies for the sandwich compounds are correlated to the barriers to rotation of the two rings. Even though the fundamental vibration cannot be observed, in certain cases it may be possible to find combination bands from which the torsional frequency can be determined. Our calculations show that previous attempts to do this for dibenzenechromium and its cation are in error.[1,3]

The vibrational energy levels for an internal rotation can be determined by solving the wave equation

$$-F\frac{d^2\Psi}{d\phi^2} + \frac{1}{2}V_n\,(1 - \cos n\phi)\Psi = E\Psi$$

where ϕ is the angle of rotation and V_n is the n-fold barrier restricting free rotation ($n = 5$ for ferrocene; $n = 6$ for dibenzenechromium). F is the internal rotation constant which is related to I_R, the reduced moment about the rotation axis, by $F = \hbar^2/2I_R$. In atomic units the I_R for unsubstituted π–Cp_2M and $(\pi$–$C_6H_6)_2M$ molecules are given by

$$I_R\,[\pi\text{–}Cp_2M] = \frac{5}{2}\,(m_C d_C^2 + m_H d_H^2)$$

and

$$I_R[(\pi\text{–}C_6H_6)_2M] = 3\,(m_C d_C^2 + m_H d_H^2)$$

where m_C and m_H are the masses of carbon and hydrogen and where d_C and d_H are the distances of the carbon and hydrogen atoms from the rotor axis (the ring centers). Evaluation of these equations yields $F[\pi\text{–}Cp_2M] = 0.301$ cm^{-1} and $F[(\pi\text{–}C_6H_6)_2M] = 0.192$ cm^{-1} for any metallocene or dibenzene-metal complex which has two parallel rings. Using a calculated value of F the wave equation can be solved for any value of V_n in order to obtain the torsional energy levels. A computer program has been written to carry out these calculations.[5] For high barrier cases solutions can also be obtained from Mathieu tables.
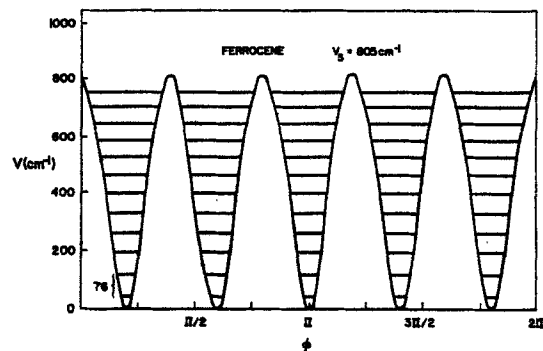

FIGURE 1 Potential energy function for the internal rotation of ferrocene. Each energy level shown has a near-degeneracy of six.

Broad line nmr spectra have suggested a barrier to internal rotation of 2.3 kcal (805 cm^{-1}) for ferrocene.[6] Using this value the torsional energy levels were calculated and are shown in Figure 1 along with the potential energy curve $V = (805/2)(1 - \cos 5\phi)$. The fundamental frequency calculated for the torsional vibration is 75.9 cm^{-1}. This has not been observed but theoretically could be obtained from combination band studies.†

† Preliminary far-infrared work in our laboratory shows no evidence for this inactive vibration.

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Figure 2 shows the calculated relationship between the torsional frequency and the barrier height for the sandwich compounds. The curves are independent of what M is since the metal atom falls on the rotor axis and does not change the value of F. The graph, therefore, makes it possible to evaluate the barrier height for any unsubstituted π-Cp$_2$M of $(\pi$-C$_6$H$_6)_2$M compound for which the torsional frequency can be determined, or vice-versa.
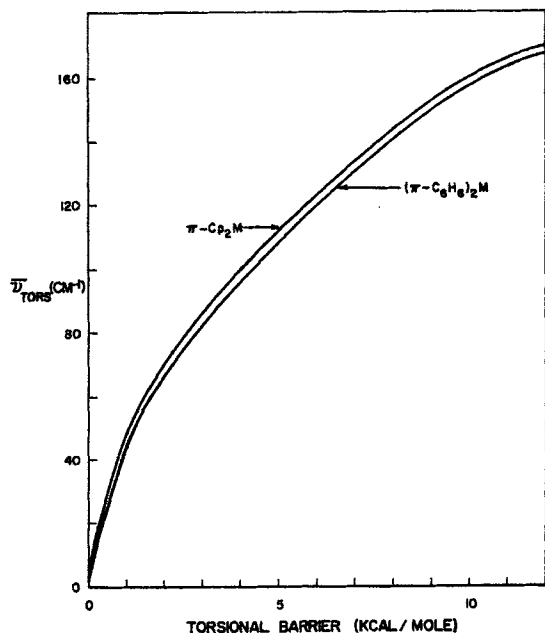

FIGURE 2 Relationship between the torsional frequency and torsional barrier of metal sandwich compounds.

In studies on chromium complexes Fritz[1] has assigned a torsional frequency of 303 cm^{-1} to $(\pi$-C$_6$H$_6)_2$Cr$^+$ from which he calculates a barrier of 1 kcal/mole. This high a frequency, however, would correspond to a barrier of 40 kcal/mole and the assignment must therefore be in error.

Likewise, a frequency of 152 cm^{-1} observed for $(\pi$-C$_6$H$_6)_2$Cr was used to estimate[3] a torsional barrier of only 0.2 kcal/mole.‡ This frequency, however, implies a highly restricted internal rotation with a barrier of 9.5 kcal/mole. For dibenzene–vanadium the torsion assigned to a band at 118 cm^{-1} (or 121 cm^{-1}) would correspond to a torsional barrier of 5.8 kcal/mole. Whether these frequencies correspond to torsional bands or lattice modes is not clear. At any rate, they certainly cannot be interpreted to support unrestricted rotation of the rings as previously proposed.

The technique described here can be used to evaluate barriers to internal rotation for derivates of the sandwich compounds as well as for other molecules using their far-infrared spectra. The value of F, however, needs to be recalculated for each molecule.

‡ The author has apparently used $F = 1.92$ cm^{-1} instead of 0.192 cm^{-1} for $(\pi$-C$_6$H$_6)_2$Cr$^+$ and $(\pi$-C$_6$H$_6)_2$Cr, thus obtaining erroneous results.

ACKNOWLEDGEMENT

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