An Electron Paramagnetic Resonance Study of Metal–Aromatic Bonding in Bis(hexamethylbenzene)iron(I)

Sir:

For metal complexes with aromatic ligands, such as ferrocene and dibenzenechromium(0), full agreement on the energetic ordering of molecular orbitals has not yet been established.[1] The hexamethylbenzene (HMB) complex of iron(II), which is isoelectronic to these complexes, takes up an additional electron into its lowest empty molecular orbital on reduction to the corresponding iron(I) complex.[2] Information about the identity of this orbital can thus be obtained by an epr study of the complex $[Fe^{I}HMB_2]^+$, the results of which we wish to report here.

In the epr spectrum of $[Fe^{I}HMB_2]^+$, three distinct absorptions are observed: $g_x = 1.865$, $g_y = 1.996$, $g_z = 2.086$ (Figure 1). This demonstrates that $[Fe^{I}HMB_2]^+$ has lost the axial symmetry of its 18-electron homologs; it must contain the two aromatic ring ligands oblique to each other. Almost certainly a Jahn–Teller effect becomes operative on insertion of the 19th electron to remove the axial symmetry. This is substantiated by the temperature dependence of the signal; its intensity diminishes drastically as the temperature is raised from 25 to 80°K, and at 90°K it has virtually disappeared. This attenuation of the resonance occurs without appreciable broadening of the absorption bands. This would correspond to the increasing population of a vibrational state where (*e.g.*, by rocking of the ligands) the Jahn–Teller distortion is dynamic. This state then must have such a short lifetime that it exhibits an extremely broad epr absorption.

Our data thus show rather unambiguously that neither the A_{1g}* nor the A_{2u}* molecular orbitals (involving the metal 4s and $4p_z$ orbitals, respectively) can be the lowest empty molecular orbital in $[Fe^{II}HMB_2]^{2+}$. Furthermore, there is rather general agreement that, at least in ferrocene, E_{1u}* (involving $4p_x$ and $4p_y$) lies still higher than A_{2u}* and that E_{2g}* (involving d_{xy} and $d_{x^2-y^2}$) and E_{1g}* (involving d_{xz} and d_{yz}) are higher than E_{2u}.[1] Thus the mere fact that the 19th electron brings about a Jahn–Teller distortion makes it highly probable that the unpaired electron is taken up by the nonbonding ligand orbitals E_{2u}.[3] The molecular orbital scheme proposed by Dahl and Ballhausen[4] for ferrocene, if applied to the iron–hexamethylbenzene system, would be in agreement with our findings.

A more detailed discussion of orbital characters and *g* values in the iron–hexamethylbenzene complex will be presented in a further publication. The epr spectrum reported here is rather similar to epr spectra recently obtained with nonheme iron complexes of biological significance;[5] possible bearings of this similarity to the mode of binding of iron in the latter will be discussed elsewhere.[6]

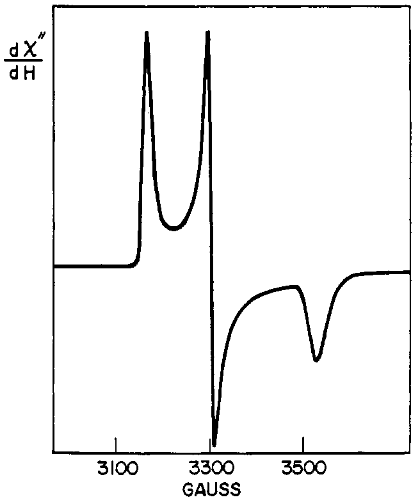

Figure 1. Epr spectrum of $[Fe^{I}HMB_2]^+$ (*ca.* 10^{-2} *M* in 50% aqueous ethanol). The spectrum was recorded with a Varian V-4502 epr spectrometer using 100-kc/sec field modulation: modulation amplitude, 6 gauss; microwave frequency, 9.234 Gc; temperature, 25°K.

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[1] For a recent discussion of the various theoretical approaches to chemical bonding in metallocenes, see M. Rosenblum, "Chemistry of the Iron Group Metallocenes," John Wiley and Sons, Inc., New York, N. Y., 1965.

[2] E. O. Fischer and F. Röhrscheid, *Z. Naturforsch.*, **17b**, 483 (1962).

[3] This is indeed the only degenerate level on the orbital scheme where metal spin–orbit coupling cannot bring about resistance to the Jahn–Teller distortion.

[4] J. P. Dahl and C. J. Ballhausen, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, 33, No. 5, (1961).

[5] G. Palmer and R. H. Sands, submitted for publication.

[6] H. Brinzinger, G. Palmer, and R. H. Sands, *Proc. Natl. Acad. Sci. U.S.*, in press.

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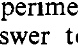
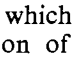
On the Nature of the Ground State of Cyclobutadiene

Sir:

One of the more interesting features surrounding the cyclobutadiene molecule concerns the nature of the ground state of the system. Simple Hückel molecular orbital theory together with application of Hund's rule, and assuming that the system possesses a square arrangement of atoms, predicts a triplet electronic ground state (I).[1] However, more elaborate calculations lead to the very different conclusion that the molecule consists of a rectangular arrangement of carbon atoms associated with alternating double and single bonds and having a singlet electronic ground state[2] (II).


I


II

The only experiment thus far which is claimed to provide an answer to the question of the electronic structure of cyclobutadiene involves the reaction of 3,4-dichlorotetramethylcyclobutene with sodium–potassium vapors at 250°. On the basis of the nature of the

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[1] J. D. Roberts, A. Streitwieser, and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

[2] M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 3255 (1965); S. Shida, *Bull. Chem. Soc. Japan*, **27**, 243 (1954); L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962), and references therein.