

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 $[\text{Fe}^{\text{I}}\text{HMB}_2]^+$, the results of which we wish to report here.

In the epr spectrum of $[\text{Fe}^{\text{I}}\text{HMB}_2]^+$, three distinct absorptions are observed: $g_x = 1.865$, $g_y = 1.996$, $g_z = 2.086$ (Figure 1). This demonstrates that $[\text{Fe}^{\text{I}}\text{HMB}_2]^+$ 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 $4p_x$ orbitals, respectively) can be the lowest empty molecular orbital in $[\text{Fe}^{\text{II}}\text{HMB}_2]^{2+}$. 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_{xy} 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 Ballhausen⁴ 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

(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.

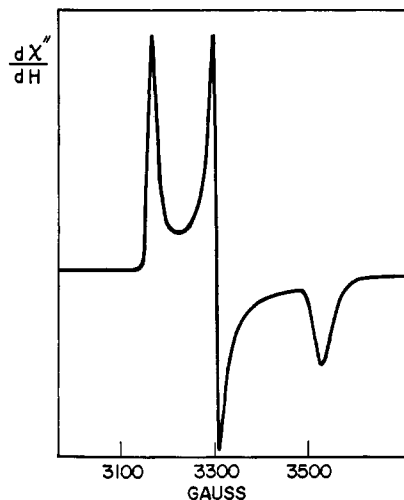


Figure 1. Epr spectrum of $[\text{Fe}^{\text{I}}\text{HMB}_2]^+$ (ca. 10^{-2} M in 50% aqueous ethanol). The spectrum was recorded with a Varian V-4502 epr spectrometer using 100-kc/sec field modulation: modulation amplitude, 6 gauss; microwave frequency, 9.234 Gc; temperature, 25°K.

similarity to the mode of binding of iron in the latter will be discussed elsewhere.⁶

Acknowledgment. This work has been supported by U. S. Public Health Service Grant GM-12176-02, and by funds of the Biophysics Research Division, Institute of Science and Technology.

(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 state² (II).



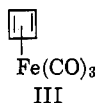
The only experiment thus far which is claimed to provide an answer to the question of the electronic structure of cyclobutadiene involves the reaction of 3,4-dichlorotetramethylcyclobutene with sodium-potassium vapors at 250°. On the basis of the nature of the

(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.

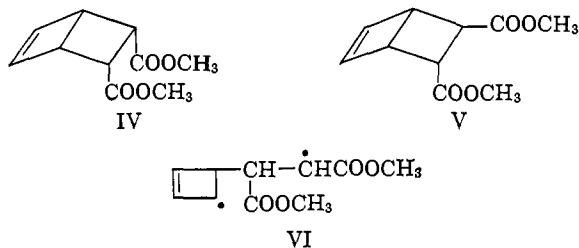
organic products produced in this reaction, Skell and Peterson deduce that cyclobutadiene possesses a triplet ground state.³ However, this conclusion can be questioned on the grounds of the nature of the experimental conditions employed in the reaction; for example, if free tetramethylcyclobutadiene is indeed involved, then reaction *via* thermally produced triplet excited species is readily conceivable.

We have previously presented evidence that degradation of cyclobutadieneiron tricarbonyl (III) with ceric ion at 0° occurs with liberation of cyclobutadiene.⁴



We now wish to report that the liberated cyclobutadiene reacts both as a diene and as a dienophile in a stereospecific manner; this supports the theory that cyclobutadiene possesses a singlet electronic ground state and, by implication, therefore has the structure II.

Degradation of the complex III at 0° in the presence of dimethyl maleate produced the *endo,cis*-dicarbomethoxybicyclohexene IV. On the other hand re-



action of cyclobutadiene with dimethyl fumarate gave the *trans*-dicarbomethoxybicyclohexene V. In both experiments vapor phase chromatography indicated the absence of the adduct produced in the other reaction. The stereochemistry of the adducts IV and V were proved through ozonolysis followed by esterification, whereupon there was produced *cis,cis,cis*-1,2,3,4-tetracarbomethoxycyclobutane and *cis,cis,trans*-1,2,3,4-tetracarbomethoxycyclobutane, respectively.⁵

The products IV and V are just those one would expect if cyclobutadiene were to act as a singlet diene in the normal Diels–Alder reaction. On the other hand, employing arguments analogous to those used by Skell and Woodworth in the determination of the spin multiplicities of carbenes,⁶ one would not expect stereospecific addition to occur if cyclobutadiene were to be a triplet. In such an event the addition to both dimethyl maleate and dimethyl fumarate should be a two-step process involving the common triplet species VI; assuming electron spin inversion and ring closure to be slow with respect to rotation about single bonds,⁷ then the same two adducts IV and V, as well as the

(3) P. S. Skell and R. J. Peterson, *J. Am. Chem. Soc.*, **86**, 2531 (1964).

(4) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

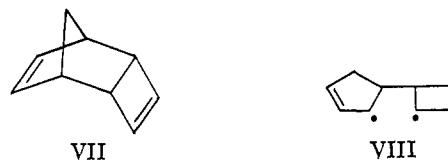
(5) We thank Professors R. Criegee and G. Griffin for providing spectral data of authentic specimens of these tetracarboxylic esters.

(6) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

(7) The basic assumption in this paper, *viz.*, that a triplet species should undergo addition reactions nonstereospecifically and reactions of singlet species should be stereospecific, while apparently widely accepted, nevertheless lacks unequivocal proof. See P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964.

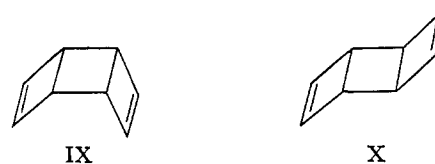
exo,cis isomer, should be produced in both reactions. This is not observed.⁸

In common with other highly strained olefins,⁹ cyclobutadiene also reacts as a dienophile and in a stereospecific manner. The reaction with cyclopentadiene at 0° produces a single C₉H₁₀ adduct, the nmr spectrum of which is consistent with the structural formula VII;¹⁰ this is the product to be expected if cyclopentadiene were to be the diene partner in the



addition. Again, if cyclobutadiene were to be a triplet, the reaction with cyclopentadiene would be expected to proceed *via* the bisallyl radical species VIII, in which case a mixture of four C₉H₁₀ hydrocarbons would reasonably be expected.

The only reaction of cyclobutadiene thus far shown to be nonstereospecific is its dimerization. When conducted in the absence of trapping agents, the degradation of complex III leads to the formation of the two dimers of cyclobutadiene, IX and X. Even in this case the *syn* isomer IX is formed preferentially (~5:1),



as would be expected from both the normal "*endo,cis*" rule in Diels–Alder additions and the related arguments recently proposed by Hoffmann and Woodward.¹¹ Since cyclobutadiene is both a very reactive diene and dienophile it is not surprising that in the dimerization the stereochemical selectivity is diminished.

(8) The products IV and V could conceivably result from 1,2-cycloadditions rather than 1,4-cycloadditions; however, this would not affect the argument pertaining to the spin multiplicity.

(9) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960).

(10) The nmr spectrum showed absorptions at τ 4.13, 4.22, 7.06, 7.43, 8.12, and 8.50 (areas 2:2:2:2:1:1); a coupling constant of 3.4 cps between the bridgehead and the allylic protons indicated an *endo* configuration.

(11) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965).

(12) The authors thank the National Science Foundation, The Army Research Office (Durham), and the Robert A. Welch Foundation for financial support. We also gratefully acknowledge a generous gift of cyclooctatetraene from Badische Anilin und Soda Fabrik.

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Biogenetic-Type Synthesis of Phenolic Compounds

Sis:

As an extension of our previous studies¹ we have continued our investigations into the construction of pyrone structures which may be visualized as "protected" polyketide chains. In this way naturally occurring phenolic compounds can be synthesized by routes

(1) T. Money, I. H. Qureshi, G. B. Webster, and A. I. Scott, *J. Am. Chem. Soc.*, **87**, 3004 (1965).