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Structure and Bonding in (Cyclobutadiene)iron Tricarbonyl

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Using an atom superposition and electron delocalization (ASED) molecular orbital theory, we determine a structure for (cyclobutadiene)iron tricarbonyl in close agreement with electron diffraction results of Davis and Speed. We find that metal overlap with and donation to the half-filled degenerate π e_g orbitals make cyclobutadiene square when complexed with rectangular distortions being energetically unfavorable. Our structures and energy surfaces are explained in terms of molecular orbital (electron delocalization) and atom superposition energy contributions to the total energy. It is found that the one-electron molecular orbital energy is alone insufficient to explain the structure of complexed cyclobutadiene.

Introduction

Although cyclobutadiene is thermodynamically unstable, it has been amply characterized theoretically[2] and experimentally.[3] (Cyclobutadiene)iron tricarbonyl, since its synthesis fifteen years ago,[4] has been characterized structurally by electron diffraction[5] and electronically by photoelectron spectroscopy[6] and molecular orbital calculations.[6b,7] We present in this paper a full structure determination and analysis of (cyclobutadiene)iron tricarbonyl using quantum mechanics. We employ the molecular orbital and total energy viewpoints in examining the distortion of stable square cyclobutadiene in the complex to the rectangular form. We use an atom superposition and electron delocalization (ASED) method[8a] which has been used as the basis of previous studies of structures and reactions of acetylene and ethylene on iron surfaces[8b,c] and (acetylene)iron carbonyl systems.[8d]

Method

From integrating the electrostatic force on a nucleus as two atoms come together forming a molecule, one obtains[8e] (if exact molecular electronic charge distributions are available) an exact binding energy E as the sum of an atom superposition repulsive contribution E_R and an electron delocalization attractive contribution E_D. E_R depends on atomic electron density functions alone, and, therefore, on atomic Slater orbitals in our work, and is easily calculated. E_D is well approximated by a one-electron molecular orbital energy obtained from a Hamiltonian[8a] similar in form to the extended Hückel Hamiltonian. (In principle E_D is exactly calculable from the molecular electron delocalization charge redistribution function, but this function is generally unavailable.) The procedure follows the same outline for polyatomic molecules, for which all pairwise contributions for E_R must be determined and then the electron orbital energy added to it. Experience has shown that E_R, which is the electrostatic energy of a bare nucleus in the presence of the other atoms, is better taken as the interaction between the nucleus of the less electronegative atom with the more electronegative atom when the molecular orbital approximation to E_D is used. The molecular orbital Hamiltonian is also a function of atomic data: Diagonal matrix elements are set equal to measured ionization potentials, and these potentials are also used in determining the off-diagonal elements.[8a]

Table I. Calculated and Experimental[4] Structures for (Cyclobutadiene)iron Tricarbonyl[a]

	calcd	exptl
Fe-CO length, Å	1.78	1.819 ± 0.010
Fe-C(ring) length, Å	2.13	2.063 ± 0.010
OC-Fe-CO angle, deg	95.5	95.5 ± 2.5
C-O length, Å	1.13	1.131 ± 0.010
C-C length, Å	1.60	1.456 ± 0.015
CH length, Å	1.15	(1.08)[b]

[a] Calculated bond lengths are determined to a precision of 0.02 Å, and the OC-Fe-CO angle is determined to 2°. [b] Estimated.

In this paper we use atomic data from references as follows: iron, carbon, and hydrogen, ref 8c; oxygen, ref 8d. Because the iron atom becomes positively changed in the complexes, we increase the 3d, 4s, and 4p ionization potentials 1.5 eV, an approximation to self-consistency as would be an outcome from ab initio calculations, which is in accord with our past experience. We use only valence atomic orbitals in the calculations for this paper, a simplification found satisfactory in most past structure analyses using the ASED theory.

Calculated Structures

A comparison of our calculated structure parameters for (cyclobutadiene)iron tricarbonyl with an electron diffraction determination by Davis and Speed[5] (Table I) shows the calculations are of good accuracy. As in past ASED studies[8b-d] the C-C bond length is overestimated, but all results are within several hundreths of an angstrom of experiment and the OC-Fe-CO angles are accurate. The staggered configuration (Figure 1) of the cyclobutadiene square (ring with respect to the iron tricarbonyl pyramid) and eclipsed forms are calculated to be equally stable with a 1 kcal/mol barrier between them. Conformation has not been resolved by electron diffraction.[5]

It is generally agreed from the theoretical viewpoint that cyclobutadiene is rectangular.[2] Our calculations concur, producing a C-C single-bond length of 1.78 Å and a C-C double-bond length of 1.47 Å, these being, respectively, 0.15 and 0.20 Å longer than obtained in a large basis set single determinent self-consistent-field calculation by Haddan and Williams.[2g] Our HCC angle of 137° agrees within 2° with that study. Our HC bond length, 1.15 Å, is 0.08 Å longer. While we could increase orbital exponents in the carbon atoms to improve our bond length determinations, doing so would not add further insight to later discussions.

We find for square cyclobutadiene C-C bond lengths of 1.60 Å, 0.17 Å greater than a MINDO/3 result of Dewar and

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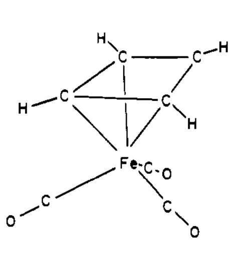

Figure 1. Calculated structure for (cyclobutadiene)iron tricarbonyl.

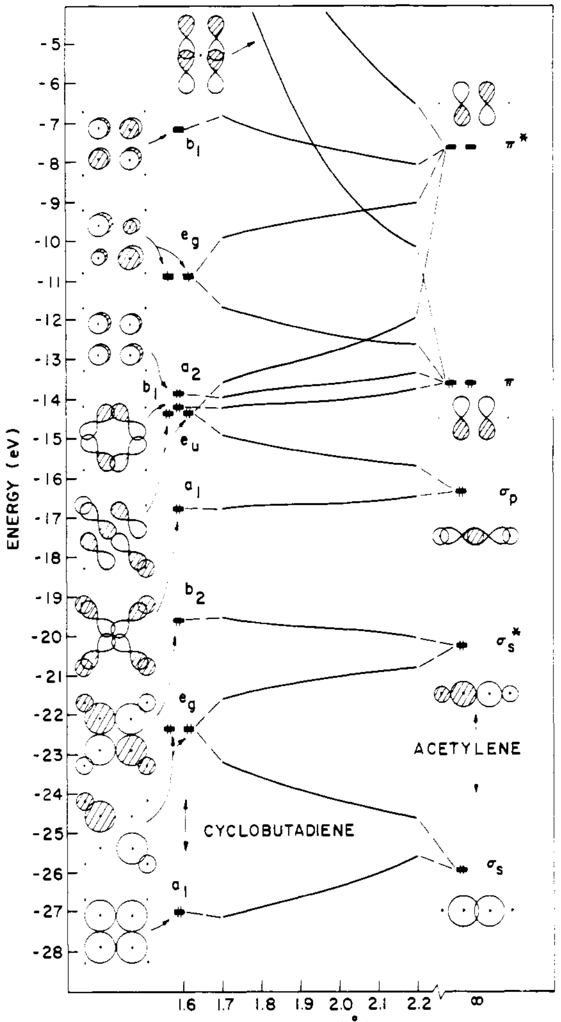

Figure 2. Energy levels for square cyclobutadiene distorting to a rectangle and becoming two acetylene molecules. The longer bond length is labeled on the abscissa. The shorter bond length is 1.47 Å for all intermediate points and 1.30 Å for acetylene.

Kollman.[2f] These authors determine that the square singlet lies 13.1 kcal/mol above the square triplet in energy. Further, they find the rectangular singlet to be 5.9 kcal/mol more stable than the square triplet. Then in the molecular orbital framework, the electron-pairing energy plus the singlet stabilization energy yields 19.0 kcal/mol. We calculate 25 kcal/mol for the energy difference of the two singlet-state structures, which is reasonable agreement between two approximate theories.

Bonding in (Cyclobutadiene)iron Tricarbonyl

In this section we discuss the structure and bonding of (cyclobutadiene)iron tricarbonyl in terms of E_R, E_D, and individual molecular orbital contributions to E_D. The behavior of the orbital energies as cyclobutadiene is pulled apart into two acetylene molecules is shown in Figure 2. Similarly, Figure 3 shows the total energy, E, the atom superposition energy, E_R, and the electron delocalization energy, E_D. E_D goes through a minimum and E_R through a maximum near the equilibrium geometry. In constrast, the complex E_D goes through a maximum and E_R through a minimum near equilibrium.

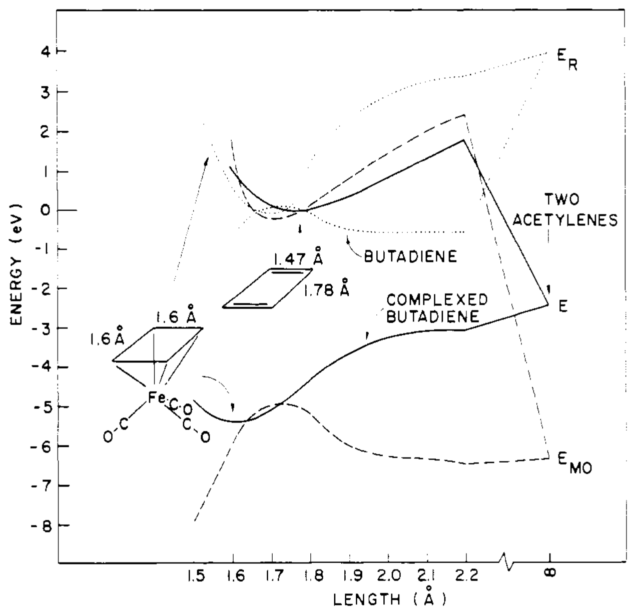

Figure 3. Behavior of atom superposition energy, E_R, electron delocalization energy, E_D, and the total energy, E, as free and complexed cyclobutadiene is distorted into a rectangle and, finally, into two uncomplexed acetylene molecules and a planar Fe(CO)$_3$ fragment.

Why do E_R and E_D exchange their roles and why is complexed cyclobutadiene square? Overall, the stabilization of the cyclobutadiene ligand is a result of bonding stabilization of the half-filled degenerate π e_g orbitals from overlap with iron d orbitals as depicted in Figure 4. This interaction was observed and discussed by Bursten and Fenske[7c] in a Fenske–Hall molecular orbital study using a fixed geometry. The degenerate orbitals accept two electrons (actually, about 1.2 electrons stay on the iron atom), and now when distortion to a rectangle lifts the degeneracy, the acetylene π^* precursor rises more rapidly in energy than the π precursor falls (Figure 5). Consequently the complex remains square. We note that we find planar iron tricarbonyl is 17 kcal/mol more stable than the pyramidal fragment and there it has a calculated decrease of 0.02 Å in the Fe–C distance. In our figures iron tricarbonyl energy levels are for the planar conformation. Energies in Figure 3 are also based on the planar conformation.

In cyclobutadiene E_R goes through a maximum near the calculated stable rectangular structure where the C–C bond lengths are 1.47 and 1.78 Å. Since E_R rises steeply as bond lengths decrease, E_R is less for the square with C–C bond lengths of 1.6 Å even though this is shorter than the average bond lengths in the rectangle. As one C–C length increases, calculations predict the other to be nearly constant as E_R decreases. Finally, C–C bonds in acetylene molecules are only 1.30 Å, so, as seen in Figure 3, E_R increases when the acetylene molecules are removed, leaving a planar Fe(CO)$_3$ fragment.

The behavior of E_D for cyclobutadiene during distortion from a square to a rectangle is complicated because of the many diverse contributions as seen in Figure 2. The σ orbitals dominate. Going to the right of equilibrium (Figure 3), bonding stabilization and antibonding destabilizations all decrease but the former at a higher rate. Going to the left, the opposite is true.

In the complex, cyclobutadiene orbital trends are perturbed, and the distortion coordinates change (Table II). Now E_R increases as the square contracts and *also* with the rectangular

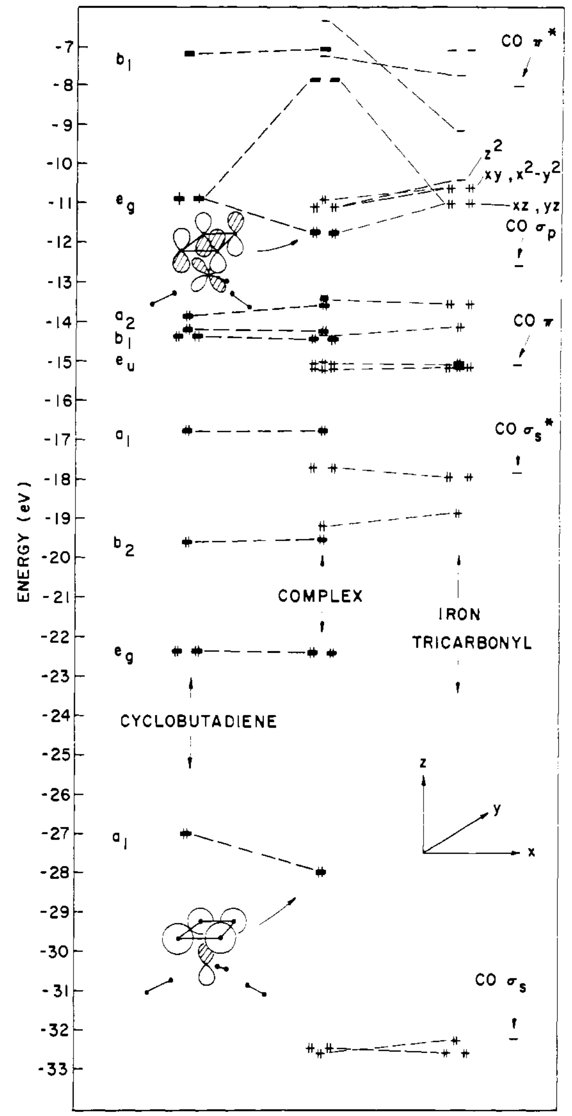

Figure 4. Energy levels for square cyclobutadiene with a C–C bond length of 1.60 Å, CO, and planar iron tricarbonyl.

Table II. Comparison of Structural Parameters for Free and Complexed Cyclopentadiene[a]

cyclobutadiene			(cyclobutadiene)iron tricarbonyl			
A, Å	B, Å	θ, deg	A, Å	B, Å	θ, deg	L, Å
1.7	1.47	137	1.60	1.60	135	1.8
1.78	1.47	137	1.70	1.60	135	1.8
1.85	1.47	137	1.80	1.47	140	1.8
2.00	1.47	140	2.20	1.35	160	1.7
2.20	1.47	140	2.50	1.35	160	1.7
10	130	180				

[a] For given C–C bond lengths A in rectangular cyclobutadiene the remaining bond lengths are calculated to be B, the B–H angle is θ, and the iron to cyclobutadiene ring distance is L.

distortion because the shorter C–C bonds shorten quickly. The rapid shortening is a consequence of E_D favoring it, for E_D drops rapidly to the left and right of equilibrium in Figure 3. Figure 5 shows how the upper σ e_u cyclobutadiene derived level and the upper π e_g derived level dominate the decrease in E_D as the C–C distance decreases. The decrease in the 1.7–2 Å range is less easily explained and is the result of an overall sum of many orbital contributions. At 2.05 Å an acetylene π type orbital drops out of the sky and empties the upper π e_g cyclobutadiene derived orbital. If initial orbital occupations are maintained, excited-state acetylene molecules are the products, and E_D will bend up again.

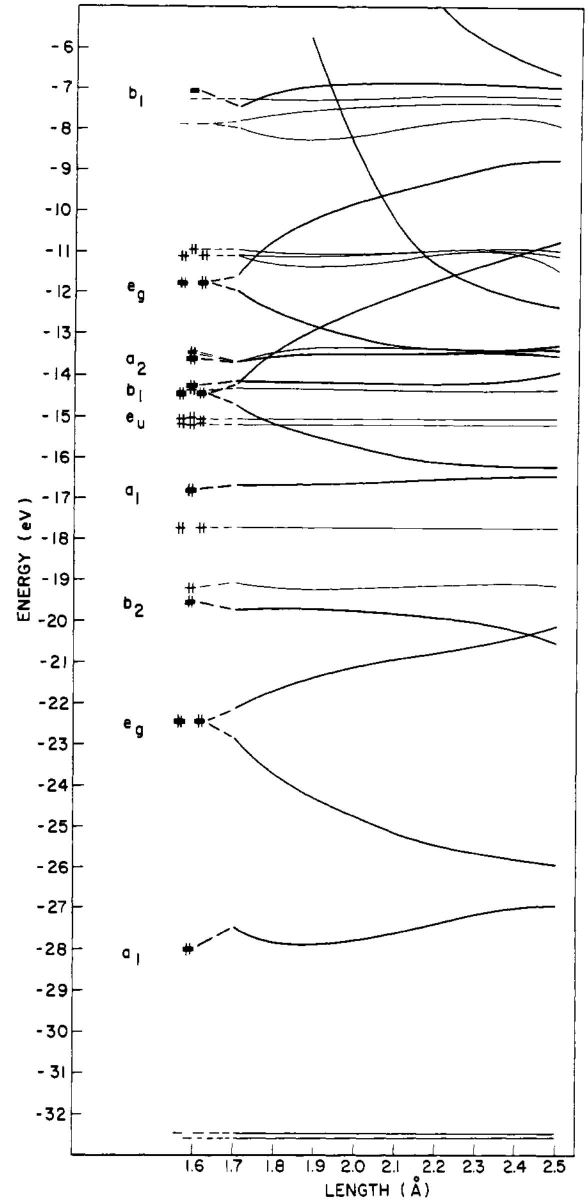

Figure 5. Energy levels for cyclobutadiene as in Figure 1 distorting to a rectangle in (cyclobutadiene)iron carbonyl.

It is of general interest that E follows the orbital energy in free cyclobutadiene and the two-body repulsion energy in the complex. *In (cyclobutadiene)iron tricarbonyl the total orbital energy fails to predict a satisfactory structure.*

In addition to stabilization of the butadiene π e_g orbital in the complex, we observe σ-framework a_1 orbital stabilization, contributing about 2 eV in our calculations. This stabilization involves negative overlap with an iron 4p orbital, as shown in Figure 4. While stabilization with negative overlap is well established, having been seen in a variety of types of theoretical studies on various systems[8b,9] and having been identified in photoelectron spectra of adsorbed unsaturated hydrocarbon molecules on a nickel surface,[10] its magnitude is sensitive to metal atom p orbital diffusiveness and is approximate. Though exponents for these orbitals are verified in ASED calculations by producing the correct magnitude for the shift of the optical

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spectrum of the metal atom in a matrix,[11] there is a degree of uncertainty about their values in complexes. It would be helpful for photoelectron studies such as in ref 5b to focus on the energy range of the σ-framework electrons to look for this effect.

Our calculations place the metal CO π^* back-bonding levels about $^3/_4$ eV above the metal–ring π-bonding levels, an ordering in agreement with the Bursten–Fenske result[7c] and with the photoelectron analysis of Hall, Hillier, Connor, Guest, and Lloyd.[6b] The Bursten–Fenske separation is about twice ours and the two theoretical results bracket the experimental measurement. These results are in contradistinction to initial-state and final-state corrected Hartree–Fock results in ref 6b, and as discussed in that reference and in ref 7c, one must go beyond using a single determinant to produce the measured results with ab initio calculations.

Concluding Comments

We have found it possible to make a full determination of the structure of (cyclobutadiene)iron tricarbonyl using the ASED quantum-mechanical theory. We find, as did past workers using an orbital method and an assumed structure,[7c] that cyclobutadiene π e_g orbitals are stabilized by overlap with a metal d orbital of similar energy. Futher, we find that the *total* molecular orbital energy does not approximate accurately the energy surface for complexed cyclobutadiene, though it does for free cyclobutadiene. Thus the pairwise atom–atom repulsion component must be included in a full structure determination (in other theories this component corresponds approximately to the nuclear repulsion energy minus electron repulsion energies, which are counted twice). However, molecular orbital theory provides the general reasons for complex formation. We also find the cyclobutadiene 2s σ-framework a_1 orbital is stabilized in an interaction with an iron 4p orbital and that this contributes substantially to the energy. Experimental identification of this class of stabilization could be interesting.

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Electronic Structure of Diiron Ferraboranes

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The electronic structure of two metallaboranes containing the $Fe_2(CO)_6$ fragment, $Fe_2(CO)_6B_2H_6$ and 1,2-$[Fe(CO)_3]_2B_3H_7$, has been explored with the use of the experimental techniques of UV–photoelectron spectroscopy and UV–visible absorption spectroscopy. Quantum chemical calculations have been carried out on these molecules with use of the extended Hückel and Fenske–Hall methods. The assigned photoelectron spectra allow a comparison of the radical cation states for the series B_5H_9, 1-$Fe(CO)_3B_4H_8$, and 1,2-$[Fe(CO)_3]_2B_3H_7$, each molecule of which formally has 14 skeletal electrons. The experimental results demonstrate significantly different charges on the iron atoms in 1,2-$[Fe(CO)_3]_2B_3H_7$, and the calculations suggest that the charge difference is required by the cage geometry. That is, in close analogy with B_5H_9, it appears that the square-pyramidal cage geometry requires greater valence orbital participation in bonding for iron in an apical position vs. a basal position. Available evidence suggests the low-energy UV–visible absorption bands of diiron ferraboranes are associated with the $Fe_2(CO)_6$ fragment and that the lowest unfilled MO is Fe–Fe antibonding in nature.

Introduction

The primary measure of the nature of chemical bonding is molecular geometry. Hence, similar geometries imply related bonding. For this reason, the hypothesis, referred to as the "borane analogy",[2] that the cage structures of boranes should serve as models for some transition-metal clusters provides not only an appealing paradigm of pedagogical value but also a method of systematically exploring the electronic properties of transition metals in a cluster environment. In the molecular orbital (MO) approximation, an observed metal cluster–borane analogy implies qualitative similarities between the MO's associated with the cluster bonding. But it must be remembered that there will be many MO's in both borane and metal cluster, not primarily associated with cluster bonding, that are different. Thus, similar cluster geometries do not imply similar physical and chemical properties. Still the borane provides a useful base point against which the behavior of the metal systems can be contrasted.

In this vein we have set out to systematically explore the five-atom cluster system with 14 skeletal bonding electrons which, with iron as the transition metal, has the general molecular formula $[Fe(CO)_3]_xB_{5-x}H_{9-x}$. We have previously presented information on the electronic structure[3] and photochemistry[4] of 1-$Fe(CO)_3B_4H_8$[5] and on the geometrical structure of 1,2-$[Fe(CO)_3]_2B_3H_7$.[6] In the following, the electronic structure of 1,2-$[Fe(CO)_3]_2B_3H_7$ and the related compound $Fe_2(CO)_6B_2H_6$ is explored with use of UV–photoelectron (PE) spectroscopy to reveal the low-lying radical cation states and UV–visible spectroscopy to reveal the low-lying excited molecular states. With the aid of the extended Hückel[7] and Fenske–Hall[8] quantum chemical methods, the experimental information is discussed and used to construct a picture of the structure and bonding in these ferraboranes

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