note that the D_{6h} structure, if it were a proper transition state, would likely have a negative activation entropy (the statistical factor is unity, therefore the only contribution to the entropy of activation would come from the vibrational-partition functions). Both MINDO/2 and valence force field methods dismiss this possibility on energetic grounds, and MINDO/2 eliminates this structure on the basis of its force constants as well. Anet and Bourn give an extensive discussion of the errors in their experiment. However, the fact that two independent nmr techniques were used to give rate constants over nearly a 100° temperature range indicates that their value of 2.8 is probably reliable.

Conclusion

We have located and characterized six of the stationary points in the cyclohexane system with the MINDO/2 semiempirical molecular orbital method. A comparison of the calculated structures with those found previously, either experimentally or theoretically, shows good overall agreement. The surprising result that the C_s structure is predicted to be slightly more stable than the C_2 structure, as well as the consistently low-activation barriers, could be an artifact of the MINDO/2 method and awaits further verification by studies on a more accurate potential-energy surface. Based on the results of the force-constant calculations, and the nearly equal energies of the C_2 and C_s structures,

we have suggested, as have Pickett and Strauss,[41] that there is effectively only one transition state. This transition state can be envisioned as encompassing a rather wide ridge on the many dimensional potential-energy surface, which would include all points along a pseudorotational coordinate connecting the C_2 and C_s structures. Furthermore, we have shown that previous calculations for the inversion have necessarily provided lower bounds to the enthalpies of activation on their respective surfaces. Finally the calculated entropy of activation, although positive, is in disagreement with presently accepted experimental values. Further work aimed at understanding the applicability and limitations of these methods in the elucidation of structures of organic transition states is in progress.

Electronic Structure of Iron Trifluoride[1]

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Abstract: *Ab initio* quantum mechanical electronic structure calculations have been carried out on the neutral molecule FeF₃. An essentially "double ζ" basis set of contracted gaussian functions was used. Calculations were carried out for three different F–Fe–F angles, 120, 109.471, and 90°. The high-spin $^6A_1'$ state is predicted to be the ground state and have a planar or nearly planar equilibrium geometry. For planar geometry, the low-spin $^2A_1'$ state is predicted to lie 7.66 eV above the high-spin state. A Walsh-like analysis is used to discuss the possible geometries of other transition-metal trifluorides. The electronic structure is further discussed on the basis of Mulliken populations, and a variety of molecular properties are reported.

For a variety of transition-metal complexes,[4–14] *ab initio* electronic structure calculations are now becoming feasible. These calculations have already considerably furthered our fundamental understanding of the electronic structure of these interesting molecules, and the future appears very bright for this area of research. The most serious criticism which can be raised of these calculations[4–14] concerns the choice of basis set. In most of the calculations, either a minimum basis set (one function per occupied atomic orbital of the separated atoms) or a slightly better than minimum basis was used. The deficiencies of such small basis

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(2) Miller Fellow.
(3) Alfred P. Sloan Fellow.
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(12) Ag⁺(C₂H₄): H. Basch, *J. Chem. Phys.*, 56, 441 (1972).
(13) CrO₈³⁻: J. Fischer, A. Veillard, and R. Weiss, *Theor. Chim. Acta*, 24, 317 (1972).
(14) Ni(C₅H₅)NO: I. H. Hillier and V. R. Saunders, *Mol. Phys.*, 23, 449 (1972).

4518

e'

a'

e''
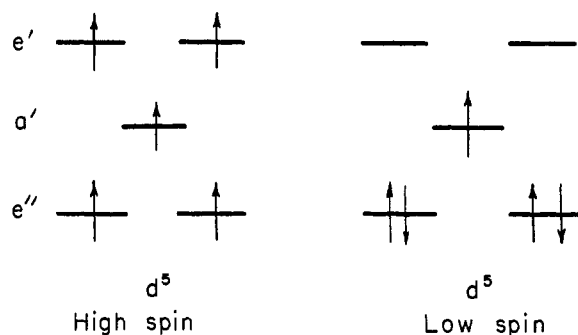
d^5 d^5
High spin   Low spin

Figure 1. Schematic representation of the electronic structure of the high- and low-spin states of planar FeF_3.

sets are well known.[4] Only in the work of Wachters and Nieuwpoort[11] on $NiF_6{}^{4-}$ and $NiFNi^{3+}$ was a true double ζ^4 quality basis used. A double ζ basis is twice the size of a minimum basis and thus includes, for example, for the F atom, two 1s functions, two 2s functions, two $2p_x$ functions, two $2p_y$ functions, and two $2p_z$ functions.

In earlier papers,[15,16] we have employed larger basis sets (double ζ or slightly more extended) to study the electronic structures of two relatively simple molecules, ZnF_2 and CaF_2. In the present work, we extend the same methods to the somewhat larger FeF_3 molecule. Our motivation in carrying out such computations is the belief that the resulting wave functions will yield properties qualitatively closer to the Hartree–Fock values than would be possible using smaller minimum or near-minimum sets. This in turn will, hopefully, lead us to an understanding of the usefulness of the Hartree–Fock approximation, when applied to transition-metal complexes.

Of the transition-metal trifluorides, from TiF_3 to CuF_3, all but NiF_3 and CuF_3 have been prepared in the laboratory.[17] However, relatively little is known about the gaseous molecules in terms of their geometries, electronic structures, and other molecular properties, e.g., dipole and quadrupole moments.[17] The geometry of the neighboring molecule ScF_3 has been the subject of two studies. Hauge, Hastie, and Margrave[18] have suggested that ScF_3 is planar, due to the absence of the ν_1 frequency in the ir spectrum of the matrix-isolated species. On the other hand, Kaiser, Falconer, and Klemperer[19] have suggested that ScF_3 is a polar molecule (possibly T shaped) based on their molecular beam electric deflection experiments. Hastie, Hauge, and Margrave[20] have also studied TiF_3 in neon and argon matrices, and their work suggests a pyramidal C_{3v} equilibrium geometry.

Rather than carrying out self-consistent-field calculations on each of the transition-metal trifluorides, a less costly and more qualitative approach was adopted. We decided to choose a single molecule, FeF_3, and

construct an *ab initio* Walsh diagram,[21] from which it might be possible to predict the geometries of the entire series of transition-metal trifluorides.

FeF_3 is a good choice for the present study since it lies about halfway through the series and is the first molecule for which each of the transition-metal d-like orbitals becomes occupied. Figure 1 shows the traditional crystal-field picture[22] of the d-orbital energies of Fe^{3+} in the field of three F^- ions. In this simple picture, the energy separation between the high- and low-spin states is given by

$$\Delta E = 2\Delta - 2P \qquad (1)$$

In eq 1, Δ is presumably the difference between the e'' and e' orbital energies, while P is a somewhat nebulous quantity called the "average pairing energy." Of course, if we know ΔE from experiment and obtain Δ from a Hartree–Fock calculation, we can deduce a semiempirical value of P.

Finally, we point out that a good deal is known about the thermochemistry of the free FeF_3 molecule. Specifically, Zmbov and Margrave[23] have determined the F_2Fe-F bond dissociation energy to be 100 kcal/molecule from mass spectrometry. Combined with the F–Fe–F dissociation energy (112 kcal/mol) and that of diatomic Fe–F (108 kcal), they[23] conclude that the atomization energy of FeF_3 is 320 kcal/mol = 13.9 eV.

Details of the Calculations

The chosen basis set of contracted gaussian functions was completely analogous to that used previously[15] for ZnF_2. For Fe, Wachters[24] (14s 9p 5d) primitive gaussian basis was contracted to (9s 5p 2d). To allow a description of the Fe 4p orbital, not occupied in the SCF wave function for the electronic ground state of the atom, an additional set of p functions with exponent $\alpha = 0.23$ was included. For the Fe atom, then, this basis is of slightly better than double ζ^4 quality. For the F atom, we chose the standard (4s 2p) Dunning contraction[25] of the Huzinaga[26] primitive (9s 5p) gaussian basis. The complete basis thus includes 69 contracted functions, obtained from 146 primitive gaussians. The most serious weakness of this basis is probably the lack of an additional set of diffuse p functions on fluorine to describe the F^- negative ion.

The calculations were performed on the Lawrence Berkeley Laboratory CDC 7600 using a version of POLYATOM[27] modified to carry out open shell SCF calculations using the OCBSE method developed by Hunt, Dunning, and Goddard.[28] Obtaining the first properly converged SCF solution was quite difficult, several different extrapolation and averaging schemes being required. However, for the remaining geometries the

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Table I. Energies (in hartrees) and Mulliken Atomic Populations for Iron Trifluoride[a]

	$\theta = 120°$ $^2A_1'$	$\theta = 120°$ $^6A_1'$	$\theta = 109.47°$ $^6A_1$	$\theta = 90°$ $^6A_1$
Total energy	−1560.5897	−1560.8711	−1560.8474	−1560.7799
Potential energy	−3120.7653	−3121.7208	−3121.6825	−3121.6259
Kinetic energy	+1560.1756	+1560.8497	+1560.8351	+1560.8460
Virial ratio (V/T)	−2.000265	−2.000014	−2.000008	−1.999958
Electronic energy	−1795.1812	−1795.4626	−1797.8093	−1804.1533
Nuclear repulsion	+234.5915	+234.5915	+236.9619	+243.3735
Fe population	24.277	24.041	24.053	24.104
F population	9.574	9.653	9.649	9.632

[a] θ is the F–Fe–F bond angle.

SCF calculations converged smoothly using the first solution as a set of starting orbitals.

All calculations reported here were carried out for a single Fe–F bond distance, namely 1.9 Å = 3.59048 bohrs. This distance was chosen on the basis of the experimental bond distances[29] for TiF₃ and CoF₃. Although it would have been interesting to have considered T-shaped geometries (see ref 19), additional computations were not economically feasible.

Energy Results

The high-spin state of planar FeF₃ is of $^6A_1'$ symmetry, while the low-spin state is of $^2A_1'$ symmetry.[30] For pyramidal FeF₃ these two symmetries become $^6A_1$ and $^2A_1$. Table I gives the calculated total energies and Mulliken population analyses. There it is seen that the planar high-spin state is predicted to lie 0.2814 hartree = 7.66 eV = 177 kcal/mol below the low-spin state. This result is consistent with the experimental observaton that iron(III) nearly always[22] forms high-spin complexes. However, it is clear[31] that the Hartree–Fock approximation will be better for the sextet state than for the doublet. Alternatively, there will be more correlation energy[31,32] associated with the $^2A_1'$ state than with the $^6A_1'$ state. Nevertheless, we doubt that this correlation energy correction will make the sextet–doublet splitting much less than 5 eV.

For the high-spin state, calculations were also carried out for tetrahedral ($\theta(F–Fe–F) = 109.47°$) and octahedral ($\theta = 90°$) bond angles. In each case, the equivalence of all F–Fe–F bond angles implies a C_{3v} geometry. At 109.47°, the calculated total energy is 0.0237 hartree = 14.9 kcal/mol higher than for the planar geometry. This energy difference is large enough to strongly suggest that FeF₃ is either planar or nearly planar. Positive confirmation of the planarity of FeF₃ would require at least one more calculation, perhaps at $\theta = 118°$. At $\theta = 90°$, the total energy lies 0.0912 hartree = 57.2 kcal/mol above the planar result.

The Mulliken populations of Table I suggest that the sextet state is somewhat more ionic than the doublet. The iron atom has a "charge" of +1.72 for the $^2A_1'$ state and +1.96 for the $^6A_1'$ state. The fact that in both cases the charge is less than the formal value 3+ is typical of *ab initio* calculations with similar basis sets.[15,16] However, the relative inability of our basis to describe F⁻ may be another factor leading to the

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(30) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967.
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(32) E. Clementi, *J. Chem. Phys.*, 38, 2248 (1963).

relatively small positive charge on iron. In addition, Table I indicates that FeF₃ becomes slightly less ionic as it is bent. The charge on Fe goes from +1.96 at $\theta = 120°$ to +1.90 at $\theta = 90°$. For the planar ground state a more complete population analysis is given in Table II.

Table II. Population Analysis for the Planar Sextet Ground State of FeF₃[a]

Orbital	Fe population s	p	d	F population s	p
1a₁'	2.000				
2a₁'	2.000				
1a₂''		2.000			
1e'		4.000			
2e'			4.000		
3a₁'			2.000		
4a₁'	1.999				0.001
2a₂''		2.000			
3e'		3.993		0.003	0.004
5a₁'	0.052		0.008	1.924	0.016
4e'		0.070	0.029	3.877	0.024
1e''			1.963		0.037
6a₁'	0.018		0.968		0.014
5e'		0.014	1.865	0.001	0.120
7a₁'	0.246		0.058	0.046	1.650
6e'		0.108	0.315	0.054	3.522
7e'		0.164	0.007	0.010	3.819
2e''			0.099		3.901
3a₂''		0.064			1.936
1a₂'					2.000
Totals	6.315	12.413	5.312	11.915	17.044
Crystal-field occupations Fe³⁺F₃⁻	6	12	5	12	18

[a] Orbitals are listed in order of increasing orbital energy.

In a simple picture, the changes in electronic structure in going from TiF₃ to CuF₃ are due to the filling of the d orbitals of the metal ion M³⁺. For FeF₃, a Walsh-like diagram for these d-like orbitals is shown in Figure 2. The numerical values of the calculated orbital energies are given in Table III. Figure 2 indicates that the calculated 1e'', 6a₁', and 5e' orbital energies all increase as the molecule becomes pyramidal. This fact, taken with our earlier prediction that FeF₃ itself is planar, allows us to predict that CoF₃, NiF₃, and CuF₃ will also be planar. Further, if the Walsh argument[21] is correct, the bending force constants of FeF₃, CoF₃, NiF₃, and CuF₃ should be progressively larger.

It should also be noted that the 8a₁ and 5e orbital energies cross somewhere between the planar and tetrahedral F–Fe–F bond angles. This means that the simple picture given in Figure 1 becomes erroneous

Table III. Orbital Energies for FeF₃[a]

Orbital C_{3v}	D_{3h}	Occupation	$\theta = 120°$ $^2A_1'$	$\theta = 120°$ $^6A_1'$	$\theta = 109.47°$ $^6A_1$	$\theta = 90°$ $^6A_1$
1a₁	1a₁'	2	−261.6750	−261.7158	−261.7118	−261.7007
2a₁	2a₁'	2	−32.2669	−32.3122	−32.3076	−32.2950
3a₁	1a₂''	2	−27.7132	−27.7941	−27.7889	−27.7754
1e	1e'	4	−27.7641	−27.7904	−27.7861	−27.7742
2e	2e'	4	−26.2955	−26.2671	−26.2530	−26.2164
4a₁	3a₁'	2	−26.2955	−26.2671	−26.2530	−26.2164
5a₁	4a₁'	2	−4.4454	−4.5118	−4.5071	−4.4947
6a₁	2a₂''	2	−2.9877	−3.0831	−3.0764	−3.0606
3e	3e'	4	−3.0232	−3.0733	−3.0693	−3.0585
7a₁	5a₁'	2	−1.5478	−1.5337	−1.5190	−1.4860
4e	4e'	4	−1.5440	−1.5293	−1.5147	−1.4756
5e	1e''	2 (4)	−0.8270	−1.0403	−1.0284	−1.0110
8a₁	6a₁'	1	−0.8180	−1.0363	−1.0322	−1.0154
6e	5e'	2 (0)		−0.9780	−0.9703	−0.9423
9a₁	7a₁'	2	−0.6616	−0.6745	−0.6547	−0.6247
7e	6e'	4	−0.6600	−0.6593	−0.6471	−0.6204
8e	7e'	4	−0.6365	−0.6304	−0.6256	−0.5932
9e	2e''	4	−0.6298	−0.6286	−0.6054	−0.5561
10a₁	3a₂''	2	−0.6468	−0.6251	−0.6191	−0.5938
1a₂	1a₂'	2	−0.6202	−0.6105	−0.5938	−0.5486

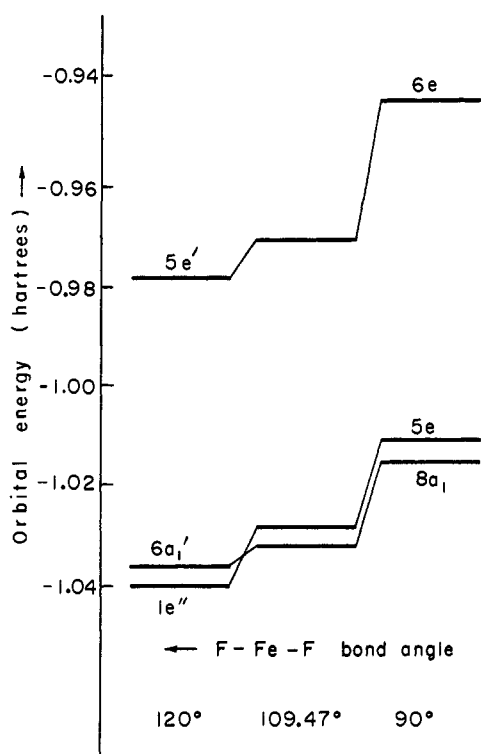[a] The occupation numbers in parentheses refer to the $^2A_1'$ state.

Figure 2. Diagram of FeF₃ orbital energies for those orbitals corresponding to the d orbitals of Fe^{3+} in a crystal-field picture.
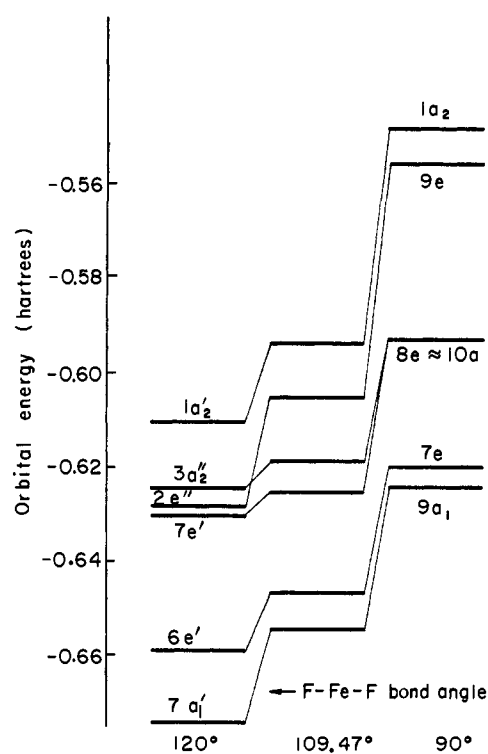

Figure 3. The six highest-lying orbital energies of FeF₃ as a function of geometry. In a rough picture these orbitals correspond to the 2p orbitals of the three F⁻ ions.

for nonplanar FeF₃. The calculated orbital energies imply that for tetrahedral and octahedral bond angles, the energetically lowest low-spin state will have orbital occupancy $8a_1{}^2 5e^3$ and thus be of ^2E symmetry.

Figure 3 shows the remaining valence orbital energies of FeF₃. These orbitals, roughly speaking, correspond to the 2 p atomic orbitals of the three F⁻ ions. We see that these ε's also increase as the molecule is bent. Therefore, even if the Fe^{3+} d-orbital energies were constant as a function of bond angle, the transition-metal trifluorides would still be expected to be increasingly planar in going from TiF₃ to CuF₃.

One of the more surprising results to be gleaned from

Table III is the fact that the half-occupied 1e'', 6a₁', and 5e' orbital energies all lie *below* the fully occupied 7a₁', 6e', 7e', 2e'', 3a₂'', 1a₂'. This is clearly contrary to intuition, which suggests that the partially occupied orbitals should have the highest orbital energies. To be certain the behavior found did not correspond to an energetically higher solution of the SCF equations, on several occasions we reoccupied the orbitals by orbital energy and began the SCF procedure again. In each case a much higher total energy resulted at first, and additional SCF iterations eventually brought us back to the original surprising SCF wave function.

Table IV. Molecular Properties of Planar FeF_3 in the $^6A_1{}'$ State[a]

Dissociation energy (eV) relative to Fe + 3F	8.5 (13.9)[b]		
Ionization potential, eV	16.6		
Second moments of the electronic charge distribution	$\langle xx \rangle$ -205.64	$\langle yy \rangle$ -205.64	$\langle zz \rangle$ -18.26
Third moments of the electronic charge distribution		$\langle xxx \rangle$ -334.48	$\langle xyy \rangle$ 334.48
Quadrupole moment tensor, 10^{-24} esu cm^2	θ_{xx}	θ_{yy}	θ_{zz}
Nuclear contribution	117.03	117.03	-234.06
Electronic contribution	-126.00	-126.00	252.00
Total	-8.97	-8.97	17.94
Octupole moment tensor, 10^{-34} esu cm^3		Ω_{xxx}	Ω_{xyy}
Nuclear contribution		555.89	-555.89
Electronic contribution		-595.12	595.12
Total		-39.23	39.23
Potential at nucleus		$\Phi(\text{Fe})$ -115.324	$\Phi(\text{F})$ -26.611
Electric field at nucleus		$E_z(\text{Fe})$ 0.00	$E_z(\text{F})$ 0.16
Diamagnetic shielding		$\langle 1/r_{\text{Fe}} \rangle$ -122.844	$\langle 1/r_{\text{F}} \rangle$ -36.748
Electric field gradient at iron	$q_{xx}(\text{Fe})$	$q_{yy}(\text{Fe})$	$q_{zz}(\text{Fe})$
Nuclear contribution	-0.29	-0.29	0.58
Electronic contribution	1.39	1.39	-2.79
Total	1.10	1.10	-2.21
Electric field gradient at fluorine	$q_{xx}(\text{F})$	$q_{yy}(\text{F})$	$q_{zz}(\text{F})$
Nuclear contribution	-1.22	0.58	0.64
Electronic contribution	0.04	0.08	-0.13
Total	-1.17	0.66	0.51

[a] Unless indicated, all quantities are given in atomic units. For the properties reported here conversion factors between atomic units and conventional units are given in Table IV of the paper by S. Rothenberg and H. F. Schaefer, *J. Chem. Phys.*, **53**, 3014 (1970). [b] Reference 23.

However, this unusual pattern of orbital energies was not without precedent; Schaefer and Bagus[33] recently found a similar situation for the MnH molecule. Furthermore, this phenomena is not simply due to the fact that open- and closed-shell orbitals are treated differently in SCF procedures.[34] That is, we are hopeful that the calculated Koopmans' theorem ionization potentials will agree qualitatively with experiment.[35] The moral of this story is that the minimization of the total SCF energy of an open-shell system need not correspond to the minimization of a sum of occupation numbers times orbital energies. More chemically, the sextet $3d^5$ structure of the Fe^{3+} ion is clearly apparent in the FeF_3 molecule, even though there are higher-lying fully occupied molecular orbitals.

One of the basic assumptions of simple molecular orbital theory is that a single orbital energy level diagram will suffice to describe the electronic structure of all the excited states, as well as the ground state, of a particular molecule. Therefore, one purpose of an *ab initio* study, such as that presented here, is to investigate the limitations of such approximations. A comparison of the orbital energies of the $^2A_1{}'$ and $^6A_1{}'$ states of FeF_3 is given in Table III. There we see that most of the corresponding orbital energies agree to within 1 or 2 eV. The serious exceptions to this pattern are the $1e''$ and $6a_1{}'$ orbital energies, which lie more than 0.2 hartree = 5.4 eV higher for the low-

spin state than for the high-spin case. Unfortunately, these are just the orbitals one would like to use in a simple discussion of the electronic structure of FeF_3. On the brighter side, the order of the $1e''$ and $6a_1{}'$ orbitals is the same in both the high-spin and low-spin calculations. Viewed in perspective, it is probably not fruitful for the theoretician to try to convince the practicing inorganic chemist to abandon his orbital energy level diagram. In fact, we must admit that such a diagram, despite its inherent inconsistencies, can be a useful tool for the classification of otherwise confusing experimental data.

Molecular Properties

As we mentioned in the introduction, almost nothing is known concerning the molecular properties of the transition-metal trifluorides. Therefore, the calculated properties of FeF_3, seen in Table IV, are true predictions. Fortunately, there have been enough comparisons[4] between *ab initio* properties (computed at roughly the present level of accuracy) and experiment to give us some confidence in the predictions made herein.

As is invariably the case, the calculated dissociation energy is less than experiment. This is a result of the correlation energy being greater for the molecule than for the separated atoms.[4] The calculated FeF_3 ionization potential (16.6 eV) may be compared with those of the Fe atom (7.9 eV), Fe^+ (16.2 eV), and Fe^{2+} (30.6 eV).

Only the nonzero moments of the electronic charge distribution are shown in Table IV. For example, it is clear from symmetry that $\langle x \rangle = \langle y \rangle = \langle z \rangle = 0$, and thus the molecule has no dipole moment. The first

(33) H. F. Schaefer and P. S. Bagus, *J. Chem. Phys.*, in press.
(34) C. C. J. Roothaan and P. S. Bagus, *Methods Comput. Phys.*, 2, 47 (1963).
(35) The referee has pointed out that for an open-shell system such as FeF_3, the molecular orbital energies seem most sensitive to occupation number, and it is possible that Koopmans' theorem may not even be qualitatively correct.

nonvanishing multipole moment, the quadrupole moment, should be independent of origin. As a test of the program, we computed θ with respect to both the Fe and F atoms. The results differed by 0.00002×10^{-24} esu cm². The octupole moment tensor of Table IV was calculated with respect to the Fe atom point charge nucleus.

The calculated potentials at the nuclei and diamagnetic shielding should be within a few per cent of experiment. The electric field $E_x(Fe)$ is zero by sym-

metry and $E_x(F)$ would be zero for an exact Hartree–Fock calculation at equilibrium geometry. Perhaps the least reliable of the predicted properties are the electric field gradient tensors. Experience has shown[4] that using comparable basis sets, calculated field gradients may differ by as much as 50% from experiment.

Conformations of Fused Cycloalkanes in Organometallic Complexes. The Crystal and Molecular Structure of Tricyclo[6.3.0.0²,⁷]undeca-3,5-dienetricarbonyliron, (C₁₁H₁₄)Fe(CO)₃[1]

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Abstract: The molecular structure of the tricarbonyliron adduct of tricyclo[6.3.0.0²,⁷]undeca-3,5-diene has been determined by X-ray crystallography. Two independent data sets, one consisting of 1539 nonzero reflections collected at $24 \pm 1°$ and the other of 3495 nonzero reflections collected at $3 \pm 1°$ were used for full-matrix least-squares refinements in which all hydrogen atoms were refined isotropically. Only slight differences, of no chemical significance, were found between the results of the two refinements. The space group is $P\bar{1}$ with $Z = 2$, and dimensions at $3 \pm 1°$ of $a = 8.390$ (3), $b = 10.700$ (4), $c = 7.981$ (2) Å; $\alpha = 107.13$ (2)°, $\beta = 97.26$ (2)°, $\gamma = 67.95$ (2)°. The unit cell edges a and b at $24 \pm 1°$ were each about 0.10 to 0.20% larger, while c was 0.13% smaller than those at 3°. The Fe(CO)₃ group is symmetrically bonded to the butadiene moiety formed by C(3) to C(6) of the tricycloolefin. The central cyclobutane ring is essentially square and planar, with the average C–C distance equal to 1.559 (2) Å, while the cyclopentane ring has an envelope conformation with a dihedral angle of 38° between the two planes. Both ring fusions are cis, and the five- and six-membered ring have an anti relationship relative to the central four-membered ring. The dimensions of the 1,3-butadieneirontricarbonyl moiety, as found in this and 11 other structures are summarized and discussed critically. In this study the three C–C distances are of equal length, while the weighted average for all structures shows the central bond to be shorter by 0.021 (2) Å. This is in contrast to the pattern in a free 1,3-butadiene group, where, for the ground state, the central, nominally single, bond is 0.09 Å longer and for the first excited state the central bond is 0.06 Å shorter.

A series of bicyclic and tricyclic polyolefins derived from the cyclooctatriene–bicyclooctadiene system by fusing on an additional four-, five-, or six-membered ring have been prepared. Complexes of these with Fe₂(CO)₆, Fe(CO)₃, Mo(CO)₃, and Mo(CO)₂ have been isolated as crystalline derivatives.[4,5] Some of these substances are of particular interest because they afford opportunities to study accurately the details of ring fusion geometry and the conformations of small and medium size rings. This is particularly true for the

series of compounds **1a–c**. The tricyclic olefins themselves, **2a–c**, vary markedly in their stability relative to their respective bicyclic tautomers, **3a–c**. The
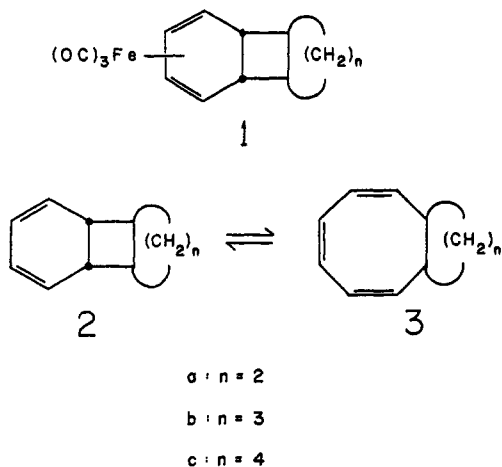
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