molecular orbitals of **2**. The four π molecular orbitals are ψ_{12}, ψ_{15}, ψ_{16}, and ψ_{17}. We find that ψ_{15} has b_2 symmetry while ψ_{16} has a_2 symmetry. Interestingly enough, the latter has a negative orbital energy ($\epsilon_{16} = -0.0498$).

Conclusion

The results of our *ab initio* calculations indicate that singlet oxyallyl is considerably less stable than cyclopropanone and appears to be at, or near, the disrotatory energy maximum. The internal angle is found to be approximately 105°. Our calculated energy difference of 83 kcal/mol is probably too high, and there are several factors that will alter ΔE for the conversion of **1** to **2**. Most important is the low-lying virtual orbital ψ_{16} in oxyallyl. A CI calculation, taking advantage of this orbital, would certainly reduce ΔE.

Our small basis set probably overestimates the strain in cyclopropanone. Hehre, Ditchfield, Radom, and Pople[21] report that their *ab initio* calculations appear to over-estimate the strain in similar ring systems.

Finally, optimizing bond distances and bond angles will influence the energies of the various species.

The calculated energy difference between cyclopropanone and allene oxide is 21 kcal/mol; since calculations that improve the energy of one would have a similar effect upon the other, this value would appear to be reasonably accurate. Therefore, even allowing for some change in the 83 kcal/mol for the opening to oxyallyl, SCF calculations predict correctly that cyclopropanone is stable with little tendency to isomerize.

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[21] W. G. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem Soc.*, **92**, 4796 (1970).

An Elementary Molecular Orbital Calculation on $U(C_8H_8)_2$ and Its Application to the Electronic Structures of $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$[1a]

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Abstract: Molecular orbital calculations have been performed on $U(C_8H_8)_2$ using the Wolfsberg-Helmholz approximation. The results of these calculations have been used to analyze the information available on $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$, with some success. The most striking prediction of the model is that the ground state of $U(C_8H_8)_2$ should have $|J_z| = 3$, which seems to be correct.

Since the first preparation of the cyclooctatetraene compounds of actinide elements,[2a] their electronic structure has been the object of considerable interest. Thus far, cyclooctatetraene compounds of Th,[2a] U,[2a] Np,[2b] and Pu[2b] have been reported, as have compounds with some substituted cyclooctatetraenes.[3] These compounds have been given the trivial names of -cene,[2a] by supposed analogy with the iron series cyclopentadienes, so one speaks of uranocene, neptunocene, and so on.

In the original report on these compounds, a qualitative discussion of their electronic structure was given, in which they were supposed to be similar to the iron series bis(cyclopentadienyl) compounds, except that the orbitals of the rings and of the metal which were involved in bonding had one more node in going around the figure axis of the molecule. These were the e_2 orbitals of the cyclooctatetraene rings and the $f_{\pm 2}$ orbitals of the metal. Increased hydrolytic stability of $U(C_8H_8)_2$, over ionic cyclooctatetraenides, was offered as evidence for the proposed covalency of the compounds.

A number of physical measurements on cyclooctatetraene compounds have subsequently appeared, which provide information about the electronic structure of the compounds. Firstly, crystallographic work has shown the compounds to be sandwich compounds, and $U(C_8H_8)_2$ has D_{8h} symmetry.[4] The magnetic susceptibilities of $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$ have been reported.[2b] Mössbauer absorption of $Np(C_8H_8)_2$ has been reported.[2]

Finally, the ^{1}H nmr of uranocene and of 1,3,5,7,1′,3′,5′,7′-octamethyluranocene has been studied[3,5] and the chemical shifts have been resolved into contact and pseudocontact contributions.

The integration of these data into a model of the electronic structure of the compounds has been only moderately successful. The Mössbauer isomer shift is most easily interpreted and suggest that the charge on Np in neptunocene is about +3.5.[2b] The susceptibility data from $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$ between 4.2 and 45°K have been fit to the Curie-Weiss law.

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[1] (a) Work performed under the auspices of the U. S. Atomic Energy Commission; (b) University of Notre Dame; (c) Lawrence Berkeley Laboratory.

[2] (a) A. Streitwieser, Jr., and U. Muller-Westerhoff, *J Amer Chem. Soc.*, **90**, 7364 (968); (b) D. G. Karraker, J. A. Stone, E. R. Jones, Jr., and N. Edelstein, *ibid.*, **92**, 4841 (1970).

[3] A. Streitwieser, Jr., D. Dempf, G. N. LaMar, D. G. Karraker, and N. Edelstein, *ibid.*, **93**, 7343 (971).

[4] A. Zalkin and K. M. Raymond, *ibid.*, **91**, 5667 (1969).

[5] N. Edelstein, G. N. LaMar, F. Mares, and A. Streitwieser, Jr., *Chem. Phys. Lett.*, **8**, 399 (1971).

$Pu(C_8H_8)_2$ is diamagnetic. $U(C_8H_8)_2$ and $Pu(C_8H_8)_2$ have magnetic moments of 2.43 and 1.81 BM, respectively. These data have been interpreted by assuming that the interaction of the metal with the rings may be described using a weak axial crystal field, a crystal field weak enough to leave J a good quantum number.[2b] This accounts for the diamagnetism of $Pu(C_8H_8)_2$, since a crystal field which leaves $J_z = \pm 4$ lowest in $U(C_8H_8)_2$ and $J_z = \pm {}^9/_2$ lowest in $Np(C_8H_8)_2$ leaves $J_z = 0$ lowest in $Pu(C_8H_8)_2$. The magnetic moments associated with the proposed ground states of $U(C_8H_8)_2$ and $Np(C_8H_8)_2$ are of the right magnitude, but rather large (3.20 and 3.27 BM, respectively, assuming LS coupling).

The nmr data, interpreted with the aid of the crystal structure to calculate the pseudocontact shifts, suggest that the contact shifts arise from spin density in the cyclooctatetraenide π orbitals, because the ring proton and methyl proton shifts are similar in magnitude but opposite in sign. The shifts correspond, however, to negative spin density in the ligand π orbitals, so a simple interpretation in terms of bonding is not possible. One finds a number of mechanisms discussed in the literature which might lead to such a distribution in spin density. Some of these are considered in ref 3. A rather strong covalency involving the $f_{\pm 2}$ orbitals, coupled with strong spin polarization by unpaired electrons in the nonbonding metal orbitals, could be responsible for the effect, but so might polarization of orbitals composed of ring π orbitals and metal 6d orbitals.

As a next step in the analysis of the electronic structure of such compounds, we have performed simple molecular orbital calculations in an attempt to estimate the energies and the compositions of the one electron orbitals derived from metal f orbitals. We have used these results to calculate the magnetic moments of the various ions in order to see if the calculations yield plausible results. We have performed these calculations two ways. Firstly, we have estimated the ground states, including interelectronic repulsion and spin-orbit coupling in a minimal way. Secondly, we have done relatively exact calculations in which we have approximated the molecular interactions by a crystal field.

Methods and Results

We estimated the energies and compositions of the one-electron orbitals by using the Wolfsberg-Helmholz method.[6] We included only metal f orbitals and ring carbon pπ orbitals.[7] In order to estimate the quantities of interest, one needs overlap integrals and valence-state ionization potentials.

We have used the ionization potentials of the various orbitals of cyclooctatetraenide estimated by Fischer.[9] There are a number of Hartree-Fock, Dirac-Slater, and Dirac-Fock calculations on the actinides available. We have used the calculations reported by Lewis, *et al.*,[10] as a starting point in the estimation of a valence state ionization potential for uranium. We will discuss this point later.

We have calculated overlaps using Dirac-Fock radial functions of U^{4+} provided in numerical form by Mann,[11] Clementi's[12] Hartree-Fock wave function for carbon, and the U-C distance from the crystal structure of $U(C_8H_8)_2$.[4] Since we did not wish to carry out a relativistic calculation, we averaged the overlaps obtained from the $f_{7/2}$ and $f_{5/2}$ wave function to get the quantities we used. The primitive overlaps we calculated were $S_{\sigma,7/2} = 0.04213$, $S_{\sigma,5/2} = 0.03973$, $S_{\pi,7/2} = 0.02973$, $S_{\pi,5/2} = 0.02759$, so the primitive overlaps used were $S_\sigma = 0.0409$, $S_\pi = 0.0287$.

Using the primitive overlaps, we have obtained the nonvanishing overlaps appearing in Table I, on the assumption that carbon-carbon overlaps could be ignored. The notation $\langle\phi_{\mu,+}|m\rangle$ means the overlap of the antisymmetric combination (denoted by +) of ring orbitals of symmetry μ (giving the number of nodes around the ring) with the metal f orbital with $m_j = m$. The most important conclusion from our attempts to estimate molecular orbital energies and compositions is already implicit in Table I. The metal ± 1 orbitals interact very little with the ring because the geometry prohibits it. The metal ± 3 orbital interaction is also small because the geometrical factors are only moderately favorable and the ring ± 3 orbitals are very loosely bound.

Table I. Nonvanishing Overlaps between Cyclooctatetraenide π Orbitals and Uranium f Orbitals

$\langle\phi_{0,-}|0\rangle = 0.0952$	$\langle\phi_{\pm 1,+}|\pm 1\rangle = \pm 0.0028$
$\langle\phi_{\pm 2,-}|\pm 2\rangle = \pm 0.0784$	$\langle\phi_{\pm 3,+}|\pm 3\rangle = \pm 0.0512$

It is customary to choose the valence state ionization potentials used in Wolfsberg-Helmholz calculations in an empirical fashion. This presumably reflects the fact that in such calculations a certain amount of interelectronic repulsion is built into the valence state ionization potentials. Axe and Burns have described their method of procedure in a rather similar problem in some detail.[13]

Given the aforementioned facts about valence state ionization potentials, it is perhaps not surprising that the ionization potentials from various calculations on free uranium atoms and ions serve poorly in these calculations. Fischer's[9] orbital energies for the various orbitals of $C_8H_8^{-2}$ are −15, −13, −9, and −5 eV. The calculated f orbital energy, even for U^0 ($5f^47s^2$) is −11.3 eV. One sees that this is rather large. Its use results in a large negative charge on the metal atom because the metal orbitals are bound more tightly than the $\mu = \pm 2$ orbitals of the ring (bound by 9 eV). There are several ways to proceed. A popular method is to make the valence state ionization potentials fit charge transfer bands. The optical spectrum of $U(C_8H_8)_2$ is known, but unassigned.[1] We have made, instead, the *ad hoc* assumption that the uranium 5f valence state ionization potential is 8.0 eV. This is rather larger than one might expect, so its use should overestimate covalency.

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(6) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," Benjamin, New York, N. Y., 1964.

(7) The optical spectrum of UCl_4 shows a broad transition which sets in at 22,500 cm^{-1}.[8] This transition could be due either to a charge transfer band or an f → d transition. However, it enables us to set a lower limit on the energy of the 6d configuration and is the reason we have used only metal f orbitals.

(8) R. McLaughlin, *J. Chem. Phys.*, **36**, 2699 (1962).

(9) R. D. Fischer, *Theor. Chem. Acta*, **1**, 418 (1963).

(10) W. B. Lewis, J. B. Mann, D. A. Liberman, and D. T. Cromer, *J. Chem. Phys.*, **53**, 809 (1970).

(11) J. B. Mann, prifate communication.

(12) E. Clementi, *IBM J. Res. Develop. Suppl.*, **9**, 2 (1969).

(13) J. D. Axe and G. Burns, *Phys. Rev.*, **152**, 331 (1966).

The eigenvalues and eigenvectors we obtain on one diagonalization of the Wolfsberg–Helmholz Hamiltonian appear in Table II. Off-diagonal elements were obtained from $H_{ij} = (H_{ii} + H_{jj})S_{ij}$.

Table II. Eigenvalues and Eigenvectors of $U(C_8H_8)_2$ Using a Valence State Ionization Potential of 8.0 eV

Symmetry label	Composition	Energy
0_1	$0.985\|\phi_{0,-}\rangle + 0.105\|0\rangle$	−15.082
0_2	$\|\phi_{0,+}\rangle$	−15.000
$\pm 1_1, \pm 1_2$	$\|\phi_{\pm 1,+}\rangle, \|\phi_{\pm 1,-}\rangle$	−13.000[a]
$\pm 2_1$	$0.878\|\phi_{\pm 2,-}\rangle - 0.414\|\pm 2\rangle$	−9.285
$\pm 2_2$	$\|\phi_{\pm 2,+}\rangle$	−9.000
$\pm 3_1$	$+0.082\|\phi_{\pm 3,+}\rangle + 0.992\|\pm 3\rangle$	−8.021
$\pm 1_3$	$\|\pm 1\rangle$	−8.000
0_3	$-0.199\|\phi_{0,-}\rangle + 0.999\|0\rangle$	−7.709
$\pm 2_3$	$0.484\|\phi_{\pm 2,-}\rangle + 0.914\|\pm 2\rangle$	−7.610
$\pm 3_2$	$\|\phi_{\pm 3,-}\rangle$	−5.000
$\pm 3_3$	$0.995\|\phi_{\pm 3,+}\rangle - 0.133\|\pm 3\rangle$	−4.946

[a] The overlap $\langle\phi_{\pm 1,+}|\pm 1\rangle$ was assumed to be exactly zero.

As one sees, the calculated levels scheme leaves the filled ring orbitals, ending with $\pm 2_2$, quite a bit below the metal orbitals ($\pm 3_1$, $\pm 1_3$, 0_3, $\pm 2_3$) in energy, and one expects a crystal field model to be useful.

In order to decide on a first-order description of the electronic state of $U(C_8H_8)_2$, we have to put two electrons into the metal orbitals and to ask for the distribution of lowest energy, including interelectronic repulsion and spin–orbit coupling, since these effects are comparable with the small differences in one-electron energies among the levels. We shall use Russell–Saunders coupling and a crystal-field model, in that we shall evaluate the interelectronic repulsion on atomic orbitals and shall include the molecular interactions only by giving the various one-electron orbitals different energies. The level scheme for the metal-like orbitals is

$$\begin{array}{rl} \pm 2 \text{———} & 3313\ \text{cm}^{-1} \\ 0 \text{———} & 2511\ \text{cm}^{-1} \\ \pm 1 \text{———} & 166\ \text{cm}^{-1} \\ \pm 3 \text{———} & 0 \end{array}$$

Since L_z is a good quantum number, we may classify states by L_z. We obtain, for the triplets

$$\begin{array}{rl} L_z = 5 & |3\alpha, 2\alpha| \\ = 4 & |3\alpha, 1\alpha| \\ = 3 & |3\alpha, 0\alpha|, |2\alpha, 1\alpha| \\ = 2 & |3\alpha, -1\alpha|, |2\alpha\ 0\alpha| \\ = 1 & |1\alpha, 0\alpha|, |2\alpha, -1\alpha|\ |3\alpha, -2\alpha| \\ = 0 & |3\alpha, -3\alpha|, |1\alpha, -1\alpha|\ |2\alpha, -2\alpha| \end{array}$$

The diagonal elements of the energy, including crystal field energy and interelectronic repulsion, are, assuming $F_2 = 200\ \text{cm}^{-1}$ and hydrogenic ratios for the F_k

$$\begin{array}{rl} L_z = 5 & -3177\ \text{cm}^{-1} \\ = 4 & -6324\ \text{cm}^{-1} \\ = 3 & -3102, -1259\ \text{cm}^{-1} \\ = 2 & -4569, +212\ \text{cm}^{-1} \\ = 1 & +2329, +1376, +1210\ \text{cm}^{-1} \\ = 0 & +2283, -4404, +4523\ \text{cm}^{-1} \end{array}$$

This is not the whole story, because there are off-diagonal elements of the interelectronic repulsion between states of the same L_z. It is clear that the ground state is $|3\alpha, 1\alpha|$ $L_z = 4$, however. The next states up are largely $|3\alpha, -1\alpha|$ $L_z = 2$ and $|1\alpha, -1\alpha|$ $L_z = 0$, a few thousand reciprocal centimeters away. The other states are quite high.

We may include spin–orbit coupling in the Hamiltonian. The state we have found to be the ground state is really an orbital doublet, $L_z = \pm 4$ and a spin triplet, of course. We may calculate the effect of spin–orbit coupling on these states and also the admixing of other states by spin–orbit coupling. We shall ignore the latter at this point, however.

The ground state $|L_z| = 4$, $S = 1$ splits, under spin–orbit coupling, into three doublets having $|J_z|$ of 5, 4, 3. The lowest is $|J_z| = 3$, corresponding to the determinants $|+3\beta, +1\beta|$, $|-3\alpha, -1\alpha|$. This has $g_{\parallel} = 4$, $g_{\perp} = 0$, so $\mu_{\text{eff}} = 2.00$ BM.

Rather than refine the simple argument we have just presented, which leads to results which are easy to visualize but are quite inaccurate, we have extended the calculation by using a program which evaluates the electrostatic, spin–orbit, and crystal field interactions.[14] We did this to see if a more exact treatment would yield the same ground state, to determine how μ_{eff} was changed, and to get a better idea of the distribution of excited states. Also, we calculated the properties to be expected for $Np(C_8H_8)_2$ and $Pu(C_8H_8)_2$, assuming the same one-electron levels.

For this calculation we fit the one-electron metal-like orbital energies to a crystal-field potential. The parameters which result are: $B_0{}^2 = 1971.4\ \text{cm}^{-1}$, $B_0{}^4 = -6636.4\ \text{cm}^{-1}$, $B_0{}^6 = 7891.4\ \text{cm}^{-1}$.[15] This effective potential method allows us to parameterize the results of the one-electron orbital calculation and at the same time treat other important interactions for an f^n configuration exactly.

The results appear in Table III. Interelectronic repulsion parameters and spin–orbit constants used were: U^{+4}, $F_2 = 206.1\ \text{cm}^{-1}$, $F_4 = 30.09\ \text{cm}^{-1}$, $F_6 = 4.516\ \text{cm}^{-1}$, $\zeta = 1638.0\ \text{cm}^{-1}$;[8] Np^{+4}, $F_2 = 211.8\ \text{cm}^{-1}$, $F_4 = 25.30\ \text{cm}^{-1}$, $F_6 = 2.96\ \text{cm}^{-1}$, $\zeta = 1985\ \text{cm}^{-1}$;[16] Pu^{+4}, $F_2 = 242.9\ \text{cm}^{-1}$, $F_4 = 34.535\ \text{cm}^{-1}$, $F_6 = 3.911\ \text{cm}^{-1}$, $\zeta = 2429.0$.[17] The LS basis states used for the $5f^2$ and $5f^3$ configurations were complete. For the $5f^4$ configuration we included only the quintets and triplets.

The ground states shown in Table III yield the following values for μ_{eff}: $U(C_8H_8)_2$, 2.24 BM; $Np(C_8H_8)_2$, 1.89 BM; $Pu(C_8H_8)_2$, 0.00 BM.

Discussion

Simple molecular orbital calculations suggest that the ground electronic states of $U(C_8H_8)_2$, $Np(C_8H_8)_2$, and $Pu(C_8H_8)_2$ are somewhat different from those predicted by a weak crystal field model,[2b] which predicts ground

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(14) This computer program was written by Dr. R. J. Mehlhorn and is partially described in his Ph.D. thesis, UCLRL-18040, 1968.

(15) Throughout this paper we have used the standard nomenclature and definitions of atomic spectroscopy. There are a number of different definitions of the crystal field parameters. We have used the definition which is most convenient in the theory of tensor operators. These definitions and nomenclature are described in B. G. Wybourne, "Spectroscopic Properties of Rare Earths," Interscience, New York, N. Y., 1965.

(16) E. R. Menzel and J. B. Gruber, *J. Chem. Phys.*, **54**, 3857 (1971).

(17) J. Conway, *ibid.*, **41**, 904 (1964).

Table III. Properties Predicted for Actinocene Compounds Using Wolfsberg–Helmholz Level Scheme and an Accurate Inclusion of Spin–Orbit Coupling and Interelectronic Repulsion[a]

$U(C_8H_8)_2$			$Np(C_8H_8)_2$			$Pu(C_8H_8)_2$		
J_z	E, cm^{-1}	$g_{\parallel}$	J_z	E, cm^{-1}	$g_{\parallel}$	J_z	E, cm^{-1}	$g_{\parallel}$
±3	−1667.3	4.479	±5/2	−1224.1	3.779	±0	−3203.7	0
±2	−464.0	3.394	±3/2	−879.1	1.463	±1	−2331.0	2.944
±4	−223.2	7.040	±9/2	−269.0	6.791	±3	−1630.1	2.694
0	192.4	0	±7/2	−208.6	6.219	±4	−565.6	5.741
±1	120.8	1.754	±1/2	276.5	0.327[b]	±2	171.5	4.796

[a] Unless noted, $g_{\perp} = 0$. [b] $g_{\perp} = 3.930$.

states having $|J_z| = 4, 9/2, 0$, respectively. The models agree that $Pu(C_8H_8)_2$ should be diamagnetic, as is observed. The magnetic moments are predicted somewhat more accurately by the results of the molecular orbital calculation. It is of interest to note that one may better reproduce μ_{eff} for $U(C_8H_8)_2$ by scaling down the crystal field splitting, a procedure which does not affect the properties of $Np(C_8H_8)_2$ or of $Pu(C_8H_8)_2$ appreciably. Table IV shows the results of scaling the potential on the properties of $U(C_8H_8)_2$. The results using a potential one-tenth the calculated potential are close to the experimental value (2.44 *vs.* 2.43 BM observed). The smaller potential leads to much closer spacing of the levels in all the compounds. The low-temperature susceptibility data have been taken to mean that only one state is populated up to 40°K or so,[2] but recent measurements have raised some questions about this point.[18] Room-temperature susceptibilities are not of much help. If one had the level scheme for $U(C_8H_8)_2$ predicted by the crystal field scaled by one-tenth, the room-temperature effective moment (at $kT = 200$ cm^{-1}) would be 2.23 BM, practically no change from that due to the ground level alone.

Table IV. Effect of Scaling of the Potential on the Properties Predicted for $U(C_8H_8)_2$

	Scale factor					
	0.1		0.5		1.0	
J_z	E, cm^{-1}	$g_{\parallel}$	E, cm^{-1}	$g_{\parallel}$	E, cm^{-1}	$g_{\parallel}$
±3	−136.3	4.877	−758.9	4.662	−1667.3	4.479
±2	5.2	3.292	−94.0	3.311	−464.0	3.394
±4	10.1	6.619	−13.0	6.771	−223.2	7.040
0	68.2	0	233.9	0	192.4	0
±1	65.0	1.681	209.4	1.772	120.8	1.754

The charge on the metal in $U(C_8H_8)_2$ is calculated to be +3.17, rather less than that deduced for $Np(C_8H_8)_2$. The electron donation to the metal is due almost entirely to the filled $\pm 2_1$ states, as Streitwieser's original model predicted.[2a] Charges were calculated in the usual way, dividing up the overlap charge equally. The use of the same molecular orbitals for $Np(C_8H_8)_2$ and $Pu(C_8H_8)_2$ as calculated for $U(C_8H_8)_2$ would give these metals the same charge.

The electronic structure predicted by the molecular orbital model is certainly consistent with a mechanism in which proton hyperfine interaction is produced by spin polarization, but one could hardly say that the calculations demonstrate the importance of this mechanism. The mechanism would require polarization of the filled $\pm 2_1$ orbitals, which are delocalized, by the two electrons in the $\pm 1_3$ and $\pm 3_1$ orbitals, which are localized on the metal. The observed proton coupling constants in these compounds are around 1 MHz,[3] which corresponds to a spin density of 0.0167 per carbon π orbital, or a total spin density of 0.1336 per molecular orbital. This is large, but not entirely unreasonable, since the orbital to be admixed by the exchange polarization, $\pm 2_3$, is only 1.2 eV away.

The molecular orbital calculations seem to have isolated the feature of the electronic structure of the actinocenes which is responsible for their ground states, the fact that the one-electron orbitals lie in two groups with ±1, ±3 below ±2, 0. The resulting ground state provides a reasonable interpretation of the properties observed in these compounds. It is impossible to say, however, whether or not the calculations are scaled correctly and this question will probably not be resolved until the optical spectra are assigned. On the computational side, we could readily predict either a larger or a smaller scale factor by changing the details of the calculation in a reasonable way. The overlaps are calculated for a +4 metal ion and uncharged C, so are probably too small. On the other hand, the assumed VSIP for uranium (8.0 eV) may well be too large.

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(18) D. G. Karraker, paper presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972. Dr. Karraker presented new magnetic measurements on $U(COT)_2$ which showed a break in the linear dependence of χ_M^{-1} *vs.* T at approximately 10°K. We suggest this data might reflect a lifting of the degeneracy of the ground state by a low symmetry crystal field.