This result can be interpreted by assuming that in pure HFP the conformation is determined by the unmodified Lys side chains protonated by the acid solvent; as a consequence, the polypeptide assumes a coil conformation which is not affected by the isomerization of the photochromic groups. Addition of a moderate amount (3-15%) of NEt_3 removes protons from Lys side chains, whose basicity depends on the isomeric composition of the photochromic moieties.[11] In the range between the transition curves of the dark-adapted and irradiated sample (Figure 2), the chain folding $\rightleftarrows$ unfolding is then controlled by the isomerization of the photochromic side chains: when these last are in the charged merocyanine form, the polypeptide chains are in the random coil arrangement; photoconversion to the apolar spiropyran form causes the macromolecules to assume a helical conformation. At NEt_3 content greater than 15%, the high concentration of a NEt_3·HFP saline complex[12] can probably exert a shielding effect of the charged side chains, allowing the polypeptide to stay in the helical conformation at any photoisomeric composition.[13]

The subject system provides a well-defined example of the combined action of light and environment on the secondary structure of polypeptides. Thus it can be considered as a macromolecular model resembling the behavior of naturally-occurring photoreceptors.[14]

Registry No. I, 55779-26-5; I (*n*-butylamide), 139168-54-0; poly(Lys·HCl) homopolymer, 26124-78-7; poly(Lys·HCl) SRU, 28575-12-4.

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(11) Addition of NEt_3 to the HFP solutions kept in the dark does not produce significative variations of the absorption spectra, thus excluding possible variations of the isomeric composition.

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Role of d and f Orbitals in the Geometries of Low-Valent Actinide Compounds. Ab Initio Studies of $U(CH_3)_3$, $Np(CH_3)_3$, and $Pu(CH_3)_3$

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Received November 21, 1991

While organoactinide compounds are traditionally characterized by high oxidation states and coordination numbers, the synthesis, chemistry, and electronic properties of low-valent actinide complexes have been receiving greater attention in recent years.[1-4] Specific examples of complexes in the AnL_3 family are represented by $U[N(SiMe_3)_2]_3$,[1] $U[CH(SiMe_3)_2]_3$,[2] and Np and Pu analogues,[3] for which cases the ligands adopt a pyramidal arrangement around the actinide. In this communication, we report the results of one of the first studies of such low-valent complexes to be carried out using ab initio electronic structure techniques. Related molecules include lanthanide species of the form LnX_3, which also adopt pyramidal geometries[5] and which have been the subject of semi-empirical theoretical investigations.[6] Transition metal MX_3 species, by contrast, can exhibit either planar or pyramidal forms, depending on the nature of the metal and the ligand.[7]

Table I. Calculated Structural Parameters for $An(CH_3)_3$ Complexes

compd	R (Å)	α (deg)[a]	β (deg)[a]	E_{rel} (kcal/mol)[b]
	Pyramidal Structures (**1**)			
UMe_3	2.543	113.1	105.6	0
$NpMe_3$	2.536	111.7	107.2	0
$PuMe_3$	2.523	110.2	108.7	0
$U[CH(SiMe_3)_2]_3$ exptl[c]	2.48	111.2	107.7	
	Planar Structures (**2**)			
UMe_3	2.586	90[d]	120[d]	3.7
$NpMe_3$	2.577	90	120	3.3
$PuMe_3$	2.558	90	120	2.4

[a] The C-An-C angle is denoted by β and the angle between the An-C bond and the 3-fold axis is denoted by α. [b] $E_{rel} = E(\text{planar}) - E(\text{pyramidal})$. [c] Reference 2. [d] Angles α and β held fixed for planar structures.

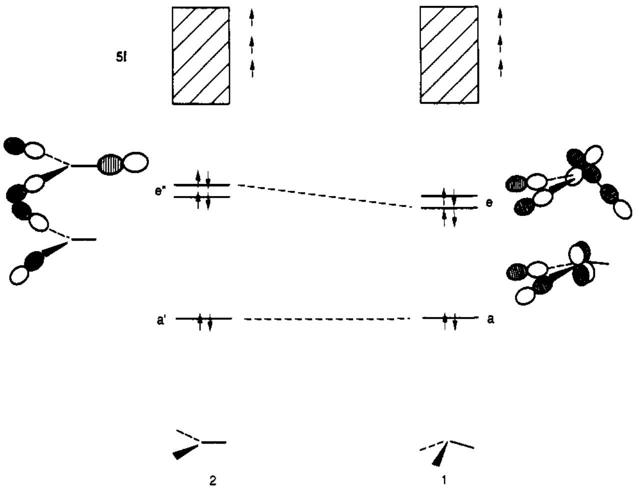

Figure 1. Schematic diagram of the changes in the bonding orbitals in UMe_3 for planar (**2**) and pyramidal (**1**) structures.

Complete active space (CAS-SCF) calculations[8] were carried out in a valence double zeta basis set employing relativistic effective core potentials (RECPs) for the actinide atoms.[9,10] In this type of calculation, the electronic structure for UMe_3, for example, can be described in terms of the open-shell configuration $[\varphi_1 \bar{\varphi}_1 \ldots \varphi_n \bar{\varphi}_n)$ $[5f^3]$, where φ_1 through φ_n denote the doubly oc-

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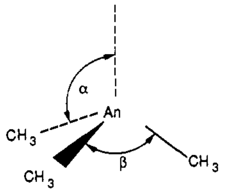
cupied orbitals and [$5f^3$] denotes all possible excitations of three high-spin electrons among the seven 5f-like orbitals. For $NpMe_3$ and $PuMe_3$, the CAS-SCF calculations involved $5f^4$ and $5f^5$ configurations, respectively.[11] For each of these three molecules there arises a dense manifold of very low-lying excited states involving $5f^n$ configurations which span several electronvolts in energy.

For the ground electronic state of each molecule, the optimum geometry for both pyramidal (**1**) and planar (**2**) $AnMe_3$ forms was determined,[12] and in each case the pyramidal structure (**1**) was found to be the stable form (Table I). The angle α corresponding to the angle between the An–C bond and the 3-fold axis was calculated to be 113.1, 111.7, and 110.2° for the series UMe_3, $NpMe_3$, and $PuMe_3$. This is in very good accord with the known X-ray structure for $U[CH(SiMe_3)_2]_3$, for which $\alpha = 111°$. The calculated An–C bond lengths decrease by 0.07 and 0.12 Å as one proceeds from U to Np to Pu. The planar structure (**2**) with C_{3h} symmetry in our model system corresponds to a transition state between the two equivalent pyramidal structures with C_3 symmetry. The barrier along the umbrella bending mode decreases in the order 3.7 (UMe_3), 3.3 ($NpMe_3$), and 2.4 ($PuMe_3$) kcal/mol, and some lengthening (0.04–0.05 Å) is noted in the bond length compared to structure **1** in each case.



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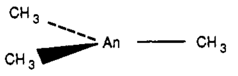

2

The result that the pyramidal structure observed experimentally can be obtained in these model compounds indicates that the geometry does not arise from steric interactions involving bulky ligands or from lattice packing interactions. The similarity of the structures with varying f-electron count also suggests that the occupancy of f orbitals is not playing a major role. The influence of spin–orbit coupling can also be discounted as a major factor since the energies of the entire manifold of $5f^4$ states for $NpMe_3$, for example, all decrease by approximately 3 kcal/mol as one proceeds along the path from planar to pyramidal geometries. While spin–orbit coupling would alter the relative ordering of states within the manifold, it would not significantly influence the overall envelope of states.

Rather, the driving force for the preference of the pyramidal structure (**1**) relative to the planar form (**2**) appears to be the involvement of 6d character in the An–C bonding orbitals as a function of bending angle. This admixture occurs primarily in the e set of U–C bonding orbitals (Figure 1). For the planar structure, the $d\pi$ and U–C bonding orbitals have e″ and e′ symmetry, respectively, and cannot interact; as one bends, the orbitals can acquire d character in the C_3 symmetry as shown in the figure. This role of d orbital participation is reflected in the increase in d_{xz} and d_{yz} populations in the Mulliken analysis from 0.04 to 0.34 electron for UMe_3 as the bending angle α increases from 90° to 113° while the overall f orbital population remains relatively constant along the bending path.

A more convincing demonstration of the role of d orbitals is provided by a series of calculations in which the d orbitals are deleted from the basis. For the case of $PuMe_3$, for example, where the calculated energy difference, E(planar) − E(pyramidal), is +2.4 kcal/mol in the full basis, this difference becomes −9.6 kcal/mol (i.e., planar lower in energy) when d functions are removed from the calculation. Similar results were obtained for the other compounds.

Acknowledgment. J.V.O. thanks the Associated Western Universities for support during his visit to Los Alamos. This work has been carried out under the auspices of the U.S. Department of Energy.

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(11) This results in 35 ($S = {}^3/_2$), 35 ($S = 2$), and 21 ($S = {}^5/_2$) states in the CAS-SCF calculation for U, Np, and Pu, respectively.

(12) The C–H distances were held fixed at 1.09 Å assuming tetrahedral geometries. The orientation of the CH_3 groups was such that the molecule had C_3 symmetry for pyramidal (**1**) forms and C_{3h} symmetry for planar (**2**) forms. The angle β is determined from α and is not a free parameter.

Optical Devices Based on Dye-Coated Superconductor Junctions: An Example of a Composite Molecule–Superconductor Device

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Received November 12, 1991

The use of molecular materials for the development of new and novel electronic devices has attracted much attention in the recent scientific literature.[1] Molecule-based devices offer prospects for enhanced sensitivity and selectivity that are not possible with conventional solid-state materials. Molecular transistors which mimic solid-state semiconductor devices have been prepared from conductive polymer, metal oxide, and redox polymer films coated on electrode surfaces.[2] In virtually all previous macromolecular devices, the active elements have been fabricated by organizing molecular systems onto a metal or semiconductor template surface. With the recent discovery of high-temperature superconductivity,[3] new opportunities exist for the development of hybrid molecule–superconductor components. In this paper, we describe methods to fabricate and demonstrate the operation of an optical sensor based on a molecular dye-coated superconductor junction.

Josephson junctions fabricated from high temperature superconductor thin films have been utilized previously to fabricate light detectors with high sensitivity (10^{-3}–10^3 V/W), fast response time (~nanosecond), and a working wavelength range from the ultraviolet to the far infrared.[4] The data presented in this paper will illustrate for the first time that a molecular dye can be utilized to enhance the sensitivity of these devices and provide them with wavelength selectivity (i.e., certain frequencies can be sensed more readily than others).

The composite dye–superconductor devices are fabricated according to the following steps. First, ~1000 Å of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ is deposited onto the surface of a clean MgO (100) substrate using the method of laser ablation.[5] Second, a superconductor microbridge ~3 mm long and ~50 μm wide is created on the film by reapplying the laser to selective regions of the film using an imaging method similar to that previously described.[6] In the final step, a dye film such as octaethylporphyrin is deposited onto the microbridge by vacuum sublimation (or spin coating). A more complete description of device fabrication methods will be published in the near future.

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