coordination geometries of the 1,2-diphenylhydrazido(2−) ligand cannot be ruled out, however.[11]

$$(C_5Me_5)_2U(CH_3)Cl + 1LiN(C_6H_5)NH(C_6H_5) \xrightarrow[-CH_4]{(C_2H_5)_2O} \underset{\mathbf{2}}{(C_5Me_5)_2U(NC_6H_5)_2} \quad (3)$$

Single crystals of **2** were grown from a concentrated toluene solution at −40 °C, and the structure was determined from diffraction data collected at −80 °C (Figure 1).[12] In the solid state, **2** is shown to be monomeric with a pseudotetrahedral coordination environment about the uranium atom. The molecule lies on a 2-fold axis of symmetry and therefore possesses one unique organoimido group and one unique pentamethylcyclopentadienyl ring. The $U–C_{ring}$ distances ($U(1)–C_{ring}$ range = 2.718 (10)–2.746 (8) Å) are not appreciably shorter than those in structurally characterized bis(pentamethylcyclopentadienyl)uranium(IV) compounds,[13] as one might expect from the relative radii of U(IV) and U(VI).[14] This may be due to interligand repulsions, although there do not appear to be any unusually close contacts between methyl groups on the two pentamethylcyclopentadienyl rings. The Cp*(centroid)–U–Cp* angle is 141.9°, which is somewhat larger than values typically found in $Cp^*_2UX_2$ complexes.[13] The short uranium–nitrogen bond length (U(1)–N(1) = 1.952 (7) Å) and nearly linear $U–N–C_{ipso}$ bond angle (U(1)–N(1)–C(11) = 177.8 (6)°) are consistent with the formulation of the ligands as organoimido groups. The uranium–nitrogen bond distance is similar to those previously determined for uranium(V) ($(MeC_5H_4)_3UNPh$: U–N = 2.019 (6) Å[3c]) and uranium(VI) ($[N(SiMe_3)_2]_3U(F)(NPh)$: U–N = 1.979 (8) Å[3a]) phenylimido complexes. The room temperature electronic absorption spectrum of **2**, recorded in toluene solution from 1500 to 300 nm, is also consistent with the assignment of a U(VI) metal center, with an absence of weak f → f transitions in the near IR. The unprecedented nonlinear (cis) orientation of the bis(imido)uranium unit (N(1)–U(1)–N(1′) = 98.7 (4)°) has no structural analogs among complexes of the isoelectronic uranyl ion, UO_2^{2+}, which have heretofore always been shown structurally and spectroscopically to be linear.[4]

The phenylimido ligands are nearly coplanar; the dihedral angle between the two phenyl rings is 6.7°. The rings rotate freely in solution, however. Only one set of phenyl ortho, meta, and para resonances is observed by ^1H and ^{13}C NMR spectroscopy at room temperature.[10] An unusual feature in the ^1H NMR spectrum of **2** is the positions of the phenylimido proton resonances at 9.26 (meta), 2.81 (ortho), and 0.72 (para), all of which are temperature invariant. We have previously reported similar chemical shifts in another U(VI) phenylimido complex.[3a] Two possible explanations have been offered for this behavior: (i) a high degree of ionic character in the metal–imide nitrogen bond is resonance delocalized to the ortho and para carbons, which, in turn shields the attached protons and shifts them to higher fields, and/or (ii) the uranium(VI) ion is behaving as a temperature independent paramagnet (TIP). We are currently examining the variable temperature magnetic behavior of **2**.

In summary, we report here the synthesis and structural characterization of the first complex of uranium(VI) displaying metal–carbon π-bonding; this is the only reported uranium(VI) organometallic complex. Further, this complex is the first example of a bis(organoimido) uranium(VI) analogue to the uranyl ion, UO_2^{2+}. The molecule displays an unusual nonlinear geometry of the two organoimido functional groups. Whether this arrangement is electronically or sterically mandated, some unusual differences in the electronic structure and reactivity of the bis(imido)- and dioxo-metal cores are likely to result. We are continuing our studies of the preparation and behavior of this new class of complexes.

Acknowledgment. We thank Dr. John M. Berg for helpful discussions and Dr. Joe D. Thompson for advice and collaboration on determining the solid-state magnetic properties of **2**. Our special thanks are extended to Dr. Alfred P. Sattelberger for technical input and advice. This work was performed under the auspices of the Division of Chemical Sciences, Office of Energy Research, U.S. Department of Energy.

Supplementary Material Available: Tables of data collection constants, atomic positional parameters, anisotropic thermal parameters, selected bond lengths and angles, hydrogen atom positions, and summary of rejected reflections for **2** (10 pages); listing of observed and calculated structure factors for **2** (9 pages). Ordering information is given on any current masthead page.

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The Central Bond $^{13}C{=}^{13}C$ Isotope Effect for Superconductivity in High-T_c β^*-$(ET)_2I_3$ and Its Implications Regarding the Superconducting Pairing Mechanism

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We report a new study, based on dc magnetization measurements, of the superconducting isotope effect for ^{13}C-substitution in the central C=C atoms of ET [bis(ethylenedithio)tetrathiafulvalene] in β^*-$(ET)_2I_3$ [or β_H-$(ET)_2I_3$], the crystallographically ordered form of β-$(ET)_2I_3$ produced by pressure.[1] Merzhanov et al. recently reported[2] that this ^{13}C-substitution yields a "giant" isotope effect in resistive studies, wherein $T_c = 8.0 \pm 0.1$ K

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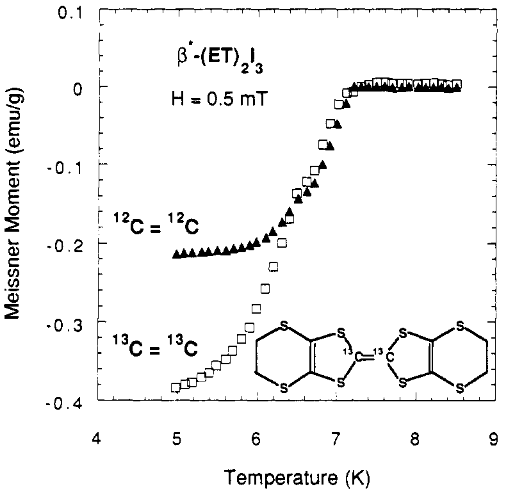

Figure 1. Superconducting transition curves determined from dc magnetization for field-cooled crystals of β^*-$(ET)_2I_3$ with $^{13}C{=}^{13}C$ in the central carbon atoms of ET (illustrated in the figure) and with natural isotopes ($^{12}C{=}^{12}C$).

(resistive transition midpoint) for β^*-$(ET)_2I_3$ with natural isotopes decreases to $T_c = 7.4 \pm 0.1$ K for the ^{13}C-substituted salt. This result affirms a theory by Yamaji[3,4] for superconducting salts of TTF-based electron-donor molecules, such as ET, that includes optical phonons of intramolecular vibrations, in addition to the acoustic phonons of conventional BCS theory,[5] as a source of mediation for superconducting pairing of charge carriers. This theory is based on the fact that the conduction-band holes in salts of TTF-based molecules strongly couple to the symmetric molecular vibrational modes composed of the C—S (~500 cm^{-1}) and C=C stretching (~1500 cm^{-1}) motions of the TTF moiety.[6-8]

The large shift reported by Merzhanov et al.,[2] $\Delta T_c = -0.6$ K, if correct, would clearly indicate that the central C=C stretching motion in the TTF moiety is a dominant exchange mechanism for superconducting pairing, because the BCS isotope effect for acoustic vibrations of the ET molecule as a whole predicts a shift, $\Delta T_c = T_c(^{12}C)[(386/384)^{-1/2} - 1] = -0.02$ K, where $T_c(^{12}C)$ refers to the salt with natural isotopes. In contrast, our study shows the absence of an isotope effect within ±0.1 K, indicating that the C=C stretching motion of ET is not a dominant exchange mechanism. Our results are consistent with those of our very recent study of the same ^{13}C isotope effect for the highest T_c ambient pressure organic superconductors, viz., κ-$(ET)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu(NCS)_2$.[9,10]

ET with natural isotopes and ET with $^{13}C{=}^{13}C$ in the central carbon atoms (see Figure 1) were synthesized in identically parallel experiments from normal CS_2 and $^{13}CS_2$ (Cambridge Isotope Laboratory, Woburn, MA) with the use of the synthetic route (site-specific for central $^{13}C{=}^{13}C$ labeling) described by Larsen and Lenoir[11] and Rae.[12] The ET used here was used also in our earlier synthesis of the κ-phase salts.[9,10] Mass spectroscopy[9] showed a 95% enrichment of ^{13}C-labeled ET, and Raman and FTIR spectra of ET exhibited the expected isotopic shifts.[9] Crystals of ambient-pressure β-$(ET)_2I_3$ were grown by previously described[13,14] electrocrystallization techniques. These crystals were investigated with the use of ESR spectroscopy[14] and showed β-type peak-to-peak line widths of 20–24 G with no α-phase contamination. No significant differences in the crystallographic lattice constants or in the low-temperature modulation vector were found between the unlabeled and ^{13}C-labeled crystals of β-$(ET)_2I_3$.[15-17]

Crystals of β^*-$(ET)_2I_3$ were produced from ambient-pressure β-$(ET)_2I_3$ with the use of the five-step recipe previously described.[18,19] The transformed β^*-$(ET)_2I_3$ crystals, stable at ambient pressure below 125 K, were transferred under liquid nitrogen to a SQUID magnetometer. First, an unlabeled crystal and a ^{13}C-labeled crystal were transformed together in the magnetometer container to β^*-$(ET)_2I_3$. The combined crystals exhibited a single superconducting transition curve with a mean-field T_c (extrapolation of the linear portion of the superconducting transition to zero moment) of 7.30 ± 0.05 K. The diamagnetic T_c is typically lower (~1 K) than the resistive T_c because the diamagnetism requires a non-zero superconducting order parameter whereas the resistance is reduced by superconducting fluctuations above T_c. These two crystals were then transformed and studied separately, yielding a mean-field T_c of 7.15 ± 0.05 K for the ^{13}C-labeled crystal and 6.95 ± 0.05 K for the unlabeled crystal ($\Delta T_c = +0.20$ K). Finally, two nearly identically shaped crystals, of mass 0.31 mg with $^{13}C{=}^{13}C$ and 0.37 mg with $^{12}C{=}^{12}C$, were transformed to β^*-$(ET)_2I_3$ and studied separately, giving the results illustrated in Figure 1. The Meissner signals of Figure 1 show a mean-field T_c of 7.09 ± 0.05 K for the $^{13}C{=}^{13}C$ crystal and 7.18 ± 0.05 K for the $^{12}C{=}^{12}C$ crystal ($\Delta T_c = -0.09$ K). The Meissner fractions at 5 K, amounting to 2.1 for the $^{13}C{=}^{13}C$ crystal and 1.2 for the $^{12}C{=}^{12}C$ crystal without correction for demagnetization, demonstrate by their large values that our transformation recipe results in an essentially complete transformation of the ambient-pressure crystals to β^*-$(ET)_2I_3$. Figure 1 exhibits a slight anomaly in the transition curves of both the $^{13}C{=}^{13}C$ and $^{12}C{=}^{12}C$ crystals near 6.5 K. The source of this anomaly, which was observed in other pressure-quenched crystals, is not understood at present, but because it occurs for both the natural and isotopically labeled crystals, it is unrelated to an isotopic shift.

We observe in these experiments a zero isotope shift for crystals transformed together and both positive and negative small isotopic shifts, $+0.20 \pm 0.07$ and -0.09 ± 0.07 K, for crystals studied separately. We therefore conclude that there is no significant isotope effect within a precision of about ±0.1 K. We also observe variations in T_c on the order of 0.2 K for salts of the same isotopic composition, although we have employed crystals that are phase-pure with a minimum of induced stresses. Thus, the results of Merzhanov et al.[2] are likely influenced by a problem of irreproducible T_c's.[20] This problem arises from the unique feature that β-$(ET)_2I_3$ crystals can have T_c's from 1.5 to 8 K, depending

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on phase purity, elapsed time, temperatures, pressures, and a variety of mechanical stresses.[14,21,22] Further isotopic substitutions are under study to examine other possibilities of phonon exchange.

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Theoretical Study of the Low-Lying Triplet and Singlet States of Diradicals: Prediction of Ground-State Multiplicities in Cyclic Analogues of Tetramethyleneethane

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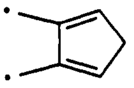
The two frontier orbitals of tetramethyleneethane (TME) are close in energy, and as a result, TME has low-lying singlet (S) and triplet (T) states.[1] The energies of these states depend strongly upon the value of the dihedral angle, α, between the planes of the two allyl groups.[2,3] Recent CI calculations[3] show that, although the S state lies below the T state for the planar (α = 0°) and perpendicular (α = 90°) structures, the T state at its potential minimum ($\alpha \approx 50°$) is about 1 kcal/mol more stable than the S state. This can explain the observation of an EPR spectrum and a linear Curie plot, due to the T state, upon photolysis of a TME precursor in a low-temperature matrix.[4]

Here, we report the results of calculations of the S–T gaps of **1–6**, in which the TME group is incorporated into ring systems, thereby precluding large deviations from planarity. On the basis of the results for TME, this should favor the S state. On the other hand, the resonance or hyperconjugative interactions present in the ring systems could favor the T state.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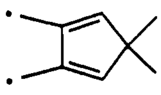
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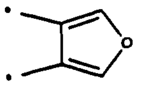
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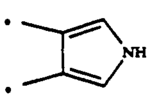
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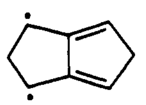
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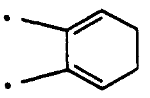
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The theoretical method used for **1–6** is identical to that employed[2,3] for TME. The geometries of the S and T states were optimized[5] using both the MCSCF(2,2)/3-21G[6] and MCSCF(6,6)/3-21G procedures,[7] assuming D_{2h} and C_2 symmetry for **5** and **6**, respectively, and C_{2v} symmetry for **1–4**. CI calculations were carried out at the MCSCF(6,6)/3-21G optimized geometries using MCSCF(6,6) MO's[8] generated from a "DZP" basis set (3s2p1d on the carbon atoms[9a] and 2s on the hydrogen atoms[9b]). The CI calculations employed one and two reference configurations for the T and S states, respectively, and permitted all single and double excitations from the valence orbitals. A Davidson-type[10] correction (DV2) was added to the CI energies to correct approximately for size-consistency errors.

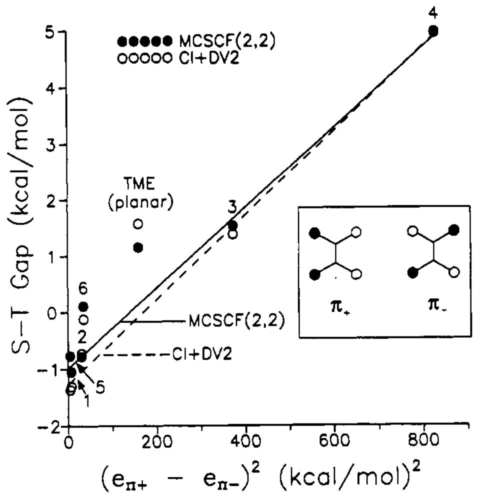

Figure 1. MCSCF(2,2) and CI+DV2 S–T energy gaps vs $(\epsilon_{\pi+} - \epsilon_{\pi-})^2$ for **1–6** and planar TME. Straight-line fits of the data for **1–5** have been included.

Both the MCSCF(2,2) and CI calculations predict T ground states for **1**, **2**, and **5** and S ground states for **3**, **4**, and planar TME.[11] For **6**, the S–T gap is predicted to be less than 0.2 kcal/mol in magnitude, favoring the T state in the CI calculations and the S state in the MCSCF(2,2) calculations. The CI orderings agree with experiment in those cases for which the multiplicity of the ground state has been determined. For example, T ground states have been reported for **2**[12] and **6**,[13] and an S ground state has been reported for **3**.[14]

The splitting energy between the π_+ and π_- frontier orbitals (shown schematically in Figure 1) is particularly important in determining whether a diradical has an S or a T ground state.[1] At zero orbital splitting, the ground state should be a triplet, and for sufficiently large orbital splittings, it will be a singlet. For planar TME, the π_+ orbital lies about 0.5 eV below the π_- orbital.[15]

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