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Computational Study of Analogues of the Uranyl Ion Containing the −N═U═N− Unit: Density Functional Theory Calculations on UO_2^{2+}, UON^+, UN_2, $UO(NPH_3)^{3+}$, $U(NPH_3)_2^{4+}$, $[UCl_4\{NPR_3\}_2]$ (R = H, Me), and $[UOCl_4\{NP(C_6H_5)_3\}]^-$

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The electronic and geometric structures of the title species have been studied computationally using quasi-relativistic gradient-corrected density functional theory. The valence molecular orbital ordering of UO_2^{2+} is found to be $\pi_g < \pi_u < \sigma_g \ll \sigma_u$ (highest occupied orbital), in agreement with previous experimental conclusions. The significant energy gap between the σ_g and σ_u orbitals is traced to the "pushing from below" mechanism: a filled−filled interaction between the semi-core uranium 6p atomic orbitals and the σ_u valence level. The U−N bonding in UON^+ and UN_2 is significantly more covalent than the U−O bonding in UON^+ and UO_2^{2+}. $UO(NPH_3)^{3+}$ and $U(NPH_3)_2^{4+}$ are similar to UO_2^{2+}, UON^+, and UN_2 in having two valence molecular orbitals of metal−ligand σ character and two of π character, although they have additional orbitals not present in the triatomic systems, and the U−N σ levels are more stable than the U−N π orbitals. The inversion of U−N σ/π orbital ordering is traced to significant N−P (and P−H) σ character in the U−N σ levels. The pushing from below mechanism is found to destabilize the U−N f_σ molecular orbital with respect to the U−N d_σ level in $U(NPH_3)_2^{4+}$. The uranium f atomic orbitals play a greater role in metal−ligand bonding in UO_2^{2+}, UN_2, and $U(NPH_3)_2^{4+}$ than do the d atomic orbitals, although, while the relative roles of the uranium d and f atomic orbitals are similar in UO_2^{2+} and $U(NPH_3)_2^{4+}$, the metal d atomic orbitals have a more important role in the bonding in UN_2. The preferred UNP angle in $[UCl_4\{NPR_3\}_2]$ (R = H, Me) and $[UOCl_4\{NP(C_6H_5)_3\}]^-$ is found to be close to 180° in all cases. This preference for linearity decreases in the order R = Ph > R = Me > R = H and is traced to steric effects which in all cases overcome an electronic preference for bending at the nitrogen atom. Comparison of the present iminato ($UNPR_3$) calculations with previous extended Hückel work on d block imido (MNR) systems reveals that in all cases there is little or no preference for linearity over bending at the nitrogen when R is (a) only σ-bound to the nitrogen and (b) sterically unhindered. The U/N bond order in iminato complexes is best described as 3.

Introduction

The study of actinide complexes remains a considerable challenge for quantum chemistry. As has been elegantly set out in several important reviews (see, for example, refs 1 and 2), the actinide elements pose special problems that are not encountered elsewhere in the periodic table. These include very large numbers of electrons (many of which occupy inner shells), the need to incorporate relativistic effects[3,4] and the energetic and spatial proximity of many valence atomic orbitals (5f, 6d, 7s, and 6p). As in many other areas of quantum chemistry, density functional methods[5] have been successfully applied to actinide systems; the reader is directed to ref 2 for an up-to-date discussion of density functional theory (DFT) in 5f element chemistry.

The chemical stability of the uranyl dication UO_2^{2+} is well-known and accounts for the ubiquity of UO_2^{2+} in uranium chemistry.[6−9] In contrast to the d block, a linear, *trans* arrangement of the oxygen atoms is always adopted,[10] and the wide variety of uranyl compounds is therefore a function of the groups that can coordinate to the uranium in the equatorial plane. The similarity between d block oxo (MO) and imido (MNR) and phosphorane iminato ($MNPR_3$) groups[11,12] prompted Denning to suggest that it may be possible to synthesize analogues of compounds of the uranyl dication in which one or both of the oxygen atoms are replaced by NPR_3 units. In the middle of the last decade he reported that his suggestion was indeed reasonable, describing the synthesis and characterization of compounds of the type $[UOCl_4\{NPR_3\}]^-$ and $[UCl_4\{NPR_3\}_2]$ (R = alkyl, aryl).[13,14] The *trans* arrangement of the O/NPR_3 and $\{NPR_3\}_2$

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(1) Pepper, M.; Bursten, B. E. *Chem. Rev.* **1991**, *91*, 719.
(2) Schreckenbach, G.; Hay, P. J.; Martin, R. L. *J. Comput. Chem.* **1999**, *20*, 70.
(3) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.
(4) Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1997**, 1.
(5) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989.
(6) Kaltsoyannis, N.; Scott, P. *The f Elements*; Oxford University Press: Oxford, U.K., 1999.
(7) Denning, R. G. *Struct. Bonding* **1992**, *79*, 215.
(8) Allen, P. G.; Bucher, J. J.; Clark, D. L.; Edelstein, N. M.; Ekberg, S. A.; Gohdes, J. W.; Hudson, E. A.; Kaltsoyannis, N.; Lukens, W. W.; Neu, M. P.; Palmer, P. D.; Reich, T.; Shuh, D. K.; Tait, C. D.; Zwick, B. D. *Inorg. Chem.* **1995**, *34*, 4797.
(9) Clark, D. L.; Keogh, D. W.; Neu, M. P.; Runde, W. In *Uranium and Uranium Compounds*; Howe-Grant, M., Ed.; Wiley: New York, 1997; p 638.
(10) It should be noted, however, that Schreckenbach et al. recently found computational evidence that the *cis* forms of $[UO_2(OH)_4]^{2-}$ are not much less stable than the *trans*. See: Schreckenbach, G.; Hay, P. J.; Martin, R. L. *Inorg. Chem.* **1998**, *37*, 4442.
(11) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.
(12) Dehnicke, K.; Strähle, J. *Polyhedron* **1989**, *8*, 707.
(13) Brown, D. R.; Denning, R. G.; Jones, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2601.
(14) Brown, D. R.; Denning, R. G. *Inorg. Chem.* **1996**, *35*, 6158.

10.1021/ic000891b CCC: $19.00

Table 1. Selected Results from Recent Calculations on UO_2^{2+}

					SCF population anal.[a]				
computational method	ref	U−O bond length/Å	$q(U)^a$	molecular orbital ordering	s	p	d	f	g
CCSD/quasi-relativistic pseudopotentials	29	1.697	+2.93	$\pi_g < \sigma_g < \pi_u < \sigma_u$					
DHF/all electron	31	1.650		$\pi_g < \sigma_u < \sigma_g < \pi_u$					
CISD/relativistic effective core potentials	30	1.699	+2.42	$\pi_g < \sigma_u < \pi_u < \sigma_g$	2.03	5.55	1.47	2.52	0.01
					3.86	8.50	0.06		
DHF + CCSD(T)/all electron	32	1.715	+3.31	$\pi_g < \pi_u \sim \sigma_g < \sigma_u$	1.93	5.59	1.10	2.07	
					4.16	9.02	0.12		
gradient-corrected DFT/quasi-relativistic frozen cores	present work	1.716	+2.88	$\pi_g < \pi_u < \sigma_g < \sigma_u$	1.79	5.49	1.20	2.63	
					4.06	8.64	0.16		

[a] Mulliken analysis. The first row of values given for the population corresponds to uranium and the second row to oxygen.

ligands in these systems led Denning to describe them as structural analogues of the uranyl dication.

In this contribution I report the results of quasi-relativistic gradient-corrected density functional theory calculations of a range of uranium compounds, all of which contain groups which may be viewed as analogues of the uranyl dication. There are several aims of this research. First, I wish to establish the extent to which the electronic structure of the "bare" iminato ions $UO(NPH_3)^{3+}$ and $U(NPH_3)_2^{4+}$ is analogous to that of UO_2^{2+} and the isoelectronic UON^+ and UN_2. Second, a rationalization is sought for the experimental observation of near-linearity along the UNP unit in uranium iminato complexes. Finally, the electronic and geometric structures of the title iminato complexes are compared with d block imido systems, with a view to probing the similarities and differences in d and f transition metal compounds of this type, particularly in relation to the bond angle at the imido/iminato nitrogen atom.

Computational and Theoretical Details

A. General Considerations. Calculations were performed with the Amsterdam density functional (ADF) program suite.[15,16] ADF type V basis sets were used for all light atoms (hydrogen, carbon, nitrogen, oxygen, phosphorus, chlorine): i.e., uncontracted triple-ζ Slater-type valence orbitals supplemented with p and d polarization functions for hydrogen and d and f functions for carbon, nitrogen, oxygen, phosphorus, and chlorine. For uranium, ADF type IV basis sets were used, which may be described as triple-ζ without polarization functions. Quasi-relativistic[17] scalar corrections—Darwin and mass−velocity—were included via the Pauli formalism, in which the first-order scalar relativistic Pauli Hamiltonian is diagonalized in the space of the nonrelativistic basis sets. The frozen-core approximation was employed, and quasi-relativistic frozen 1s and 2p cores (calculated by the ADF auxiliary program "Dirac") were used respectively for carbon, nitrogen, and oxygen and for phosphorus and chlorine. For uranium the size of the frozen core was varied, as is discussed in the main text, but was most commonly up to and including the 5d orbitals, leaving four s, three p, three d, and three f valence functions. The local density parametrization of Vosko, Wilk, and Nusair[18] was employed in conjunction with Becke's gradient correction[19] to the exchange part of the potential and the correlation correction due to Perdew.[20] Mulliken population analyses were performed.[21] The ADF numerical integration parameter was set to 6.0 in all calculations, and the energy gradient convergence criterion was set to 10^{-5} au/Å in all geometry optimizations. The calculations were performed on DEC 433au workstations and the EPSRC's "Columbus/Magellan" central computing facility.

B. Energy Decomposition Scheme. The terms "electronic effect" and "steric effect" are often used by chemists to rationalize molecular structure, bonding, and reactivity, though the precise definition of electronic and steric is in many cases unclear. ADF includes an energy decomposition scheme in which the electronic and steric contributions to the total molecular bonding energy have rigorous, explicit definitions. As I shall make use of this scheme in this article, it is important that I set out exactly what I mean by "electronic" and "steric".

ADF defines the total molecular bonding energy as the energy difference between the molecular fragments in their final positions and at infinite separation. These molecular fragments may be individual atoms or groups of atoms, though in the present study only atomic fragments are considered.[22] These fragments are placed at their positions within the molecule. At this point there is an electrostatic interaction between them, comprising the nucleus/nucleus, nucleus/electron, and electron/electron Coulombic interactions. Next it is ensured that the overall molecular wave function satisfies the Pauli principle. This is done by requiring that the one-electron orbitals of the combined fragments form a correct single-determinantal wave function. It is extremely unlikely, however, that this will be the case for the fragment orbitals when the fragments are simply placed at their positions within the molecule, because the orbitals on the different fragments will not be orthogonal to one another. Thus, the next step is to orthogonalize the occupied fragment orbitals to obtain a correct single-determinantal, antisymmetrized molecular wave function. This will result in a change in the molecular charge density, and the accompanying energy change is known as the Pauli repulsion. The steric interaction in ADF is defined as the combination of the electrostatic interaction and the Pauli repulsion and may be thought of as the energy of interaction between the fragments when none of the fragments can change in response to the presence of the others and no electron transfer can take place.

The final part of the process is to allow the fragment orbitals to relax to self-consistency. This interaction energy between the orbitals of the various fragments is defined as the electronic (or orbital) interaction within ADF and is computed using the transition state procedure first developed by Ziegler and Rauk.[23,24]

C. Neglect of Spin−Orbit Effects. In the present work only scalar relativistic effects have been included; i.e., spin−orbit coupling has not been taken into account. The justification for this approach is that all of the systems studied are closed shell, with the uranium atom being formally in its group valence (i.e., +6). As a check of this approach, a spin−orbit single-point calculation was performed at the optimized geometry of UO_2^{2+} (given in Table 1). The results are not reported here but are extremely similar to the scalar relativistic data, the only difference being a small (ca. 0.1 eV) splitting of the components of the π molecular orbitals.

Results and Discussion

A. Valence Electronic Structure. (i) UO_2^{2+}, UON^+, and UN_2.

The electronic structure of the uranyl dication has been

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(15) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.

(16) ADF2.3; Department of Theoretical Chemistry, Vrije Universiteit, Amsterdam, 1997.

(17) Ziegler, T.; Tschinke, V.; Baerends, E. J.; Snijders, J. G.; Ravenek, W. *J. Phys. Chem.* **1989**, *93*, 3050.

(18) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(19) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098.

(20) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822.

(21) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.

(22) For a discussion of the use of atomic fragments in density functional calculations, see: Baerends, E. J.; Branchadell, V.; Sodupe, M. *Chem. Phys. Lett.* **1997**, *265*, 481.

(23) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(24) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.

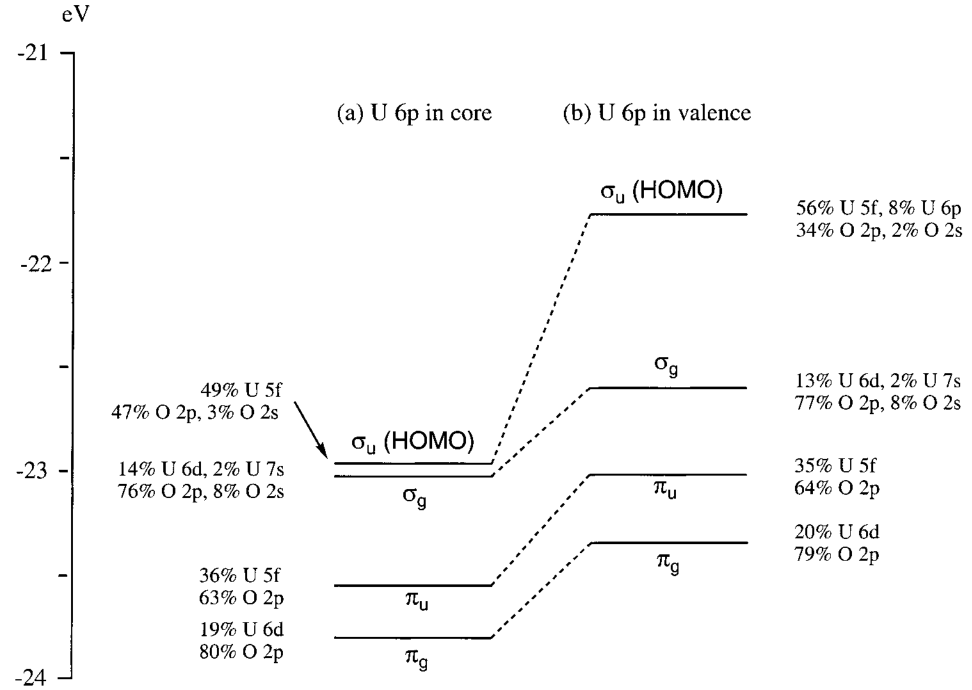

Figure 1. Valence molecular orbital energy level and composition diagrams for UO_2^{2+} calculated with the uranium 6p atomic orbitals (a) as part of the uranium frozen core and (b) as freed to participate in the valence electronic structure.

addressed many times by many workers using both experimental and theoretical techniques (see, for example, refs 1, 7, and 25–32). My purpose in revisiting it here is primarily to facilitate comparison with the results of calculations on the title iminato complexes (see section A(ii) below), and thus only those features of UO_2^{2+} relevant to the iminato work will be discussed. UN_2 and UON^+, both of which are isoelectronic with UO_2^{2+} and which have obvious relevance to the nitrogen-based iminato complexes, will also be discussed at this juncture.

It is generally agreed that UO_2^{2+} has a closed-shell singlet ground state with 12 valence electrons (coming from the oxygen 2p and uranium 5f, 6d, and 7s atomic orbitals (AOs)) and that these electrons are accommodated in four molecular orbitals (MOs), of π_g, π_u, σ_g, and σ_u symmetries (in $D_{\infty h}$ point group notation). What is less clear-cut is the ordering of these four MOs. In his 1992 review of actinyl electronic structure,[7] Denning put together the results of the experimental studies that had been performed on the uranyl dication up to that point and concluded that the ordering is $\pi_g \approx \pi_u < \sigma_g \ll \sigma_u$ (highest occupied MO). Table 1 collects a representative sample of the results of recent ab initio calculations on UO_2^{2+}, from which it may be seen that there is still no agreement as to the valence MO ordering. My starting point for the present work was therefore to establish how modern Kohn–Sham density functional methods fare in addressing the MO structure of UO_2^{2+}, with the dual aims of verifying (or otherwise) the experimentally determined MO ordering and subsequently to establish the origin of the comparatively large energy difference between the σ_u HOMO and the other valence energy levels.

Before turning to the results of the present calculations, it is worth taking a moment to explore why the σ_u MO should be significantly less stable than the π_g, π_u, and σ_g orbitals. Several explanations have been put forward, including (a) the high nodality of the uranium f_σ AO which gives rise to extensive overlap cancellation with the oxygen p_σ orbitals, such that the σ_u MO is virtually nonbonding,[33] and (b) a filled–filled interaction between the σ_u MO and the lower lying (semi-core) uranium 6p AOs which destabilizes the σ_u level. This latter explanation has been termed the "pushing from below" mechanism.[1,34]

The UO_2^{2+} valence MO energies and compositions calculated in the present study are shown in Figure 1. Two separate calculations have been performed. In one calculation the 6p AOs were included in the frozen core of the uranium atom, while in the second the uranium 6p AOs are freed to take part in the valence electronic structure. There are two main points to note from Figure 1. First, the valence MO ordering is in both cases as suggested by Denning,[7] with the π MOs below the σ and with a σ_u HOMO. Second, the gap between the σ_g and σ_u MOs with the uranium 6p AOs in the frozen core is very small. In contrast, the freeing up of the uranium 6p orbitals to participate in the valence electronic structure results in a very significant destabilization of the σ_u MO relative to the other valence levels. Indeed, the right-hand side of Figure 1 is strongly reminiscent of Figure 17 of ref 7.

The alternative explanation—poor U f_σ/O p_σ overlap—is not supported by the present calculations. Examination of the symmetrized fragment orbital overlap matrix in both calculations (uranium 6p in core and in valence) shows that overlap between the uranium valence AOs and the oxygen p levels decreases in the order $f_\sigma > f_\pi > d_\pi > d_\sigma$. I therefore suggest that the present calculations provide good evidence that it is the pushing from below mechanism that is responsible for the relative position of the σ_u HOMO in UO_2^{2+}.

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(25) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1980**, *19*, 2656.
(26) Walch, P. F.; Ellis, D. E. *J. Chem. Phys.* **1976**, *65*, 2387.
(27) Pyykkö, P.; Zhao, Y. *Inorg. Chem.* **1991**, *30*, 3787.
(28) Pyykkö, P.; Li, J.; Runeberg, N. *J. Phys. Chem.* **1994**, *98*, 4809.
(29) Cornehl, H. H.; Heinemann, C.; Marcalo, J.; Pires de Matos, A.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 891.
(30) Zhang, Z.; Pitzer, R. M. *J. Phys. Chem. A* **1999**, *103*, 6880.
(31) Dyall, K. G. *Mol. Phys.* **1999**, *96*, 511.
(32) de Jong, W. A.; Visscher, L.; Nieuwpoort, W. C. *J. Mol. Struct.* (*THEOCHEM*) **1999**, *458*, 41.
(33) Belford, R. L.; Belford, G. *J. Chem. Phys.* **1961**, *34*, 1330.
(34) Jørgensen, C. K.; Reisfeld, R. *Struct. Bonding* **1982**, *50*, 121.

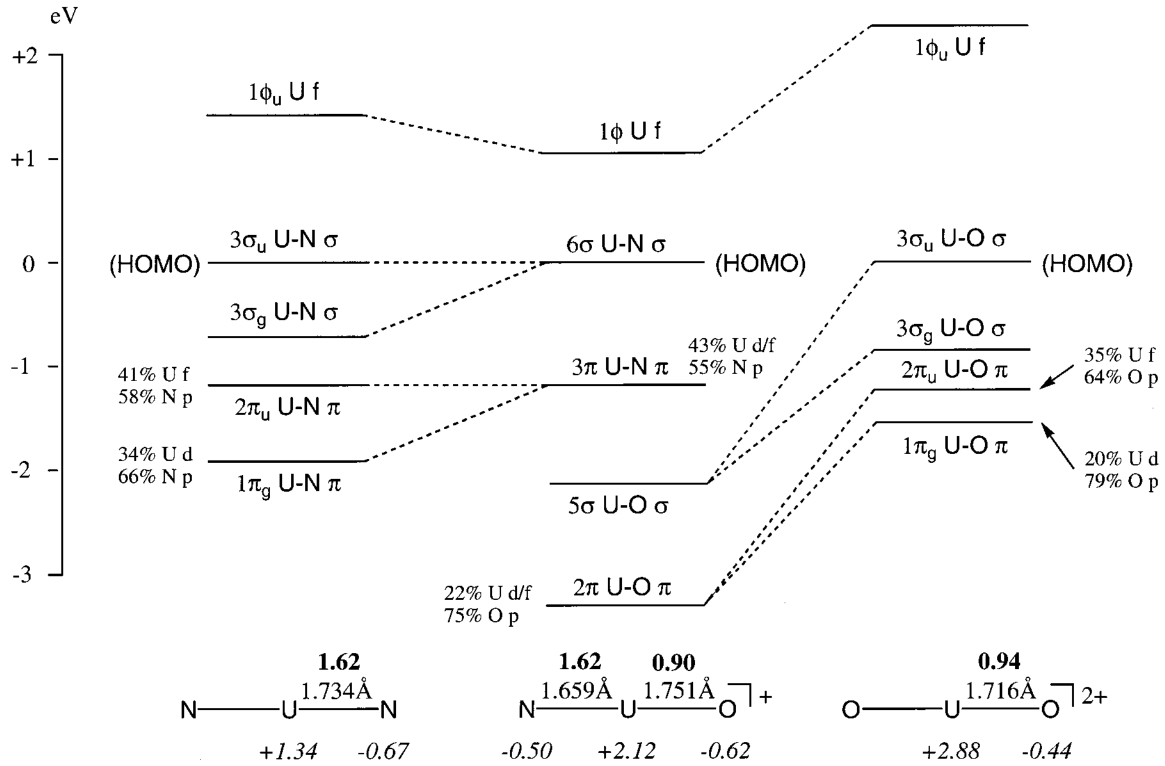

Figure 2. Valence molecular orbital energy level and composition diagrams for UN_2, UON^+, and UO_2^{2+}. The energy of the highest occupied molecular orbital has been arbitrarily set to 0 eV in all cases for comparative purposes. See the text for a description of the boldface/plain text/italic notation.

The composition of the σ_u HOMO also lends weight to the pushing from below mechanism. Comparison of the composition of the valence MOs in the two UO_2^{2+} calculations (Figure 1) shows that the π_g, π_u, and σ_g MOs are largely unperturbed by the inclusion or otherwise of the uranium 6p AO in the frozen core. However, the composition of the σ_u MO is significantly different between the two calculations, with enhanced uranium f and reduced oxygen 2p in the 6p-in-valence calculation and a crucial 8% uranium 6p contribution in this case. The participation of the uranium 6p AO in the σ_u HOMO leaves a partial hole in the uranium 6p levels. This is seen in the population analysis data given in Table 1, in which the uranium 6p population is reduced from an atomic 6.0 to 5.49 in the molecular calculation. This effect, which has also been observed by Zhang and Pitzer[30] and de Jong et al.[32] (and, indeed, by Walch and Ellis[26] and Tatsumi and Hoffmann[25]) has been used to explain the inverse *trans* influence in $[UOCl_5]^-$.[7]

I turn now to linear UON^+ (which was first studied theoretically by Pyykkö et al.[28] and subsequently synthesized by Heinemann and Schwarz[35]) and UN_2 in their singlet closed-shell ground states, species which are isoelectronic with UO_2^{2+} and whose nitrogen ligands make them an obvious choice for comparison with the title iminato complexes. The valence electronic structures of UON^+ and UN_2 are shown in Figure 2, together with that of UO_2^{2+} (taken from the right-hand side of Figure 1) for comparative purposes. As direct comparison of the eigenvalues of UO_2^{2+}, UON^+, and UN_2 is precluded by the different charges of the three species, I have arbitrarily set the energy of the HOMO to 0 eV in each case and plotted the other orbitals relative to this zero. At the bottom of the figure are given three other pieces of calculational data; the optimized bond lengths (Å) are shown in plain text, the Mulliken overlap populations (e^-) are in boldface, and the atomic charges are italicized.

It is clear that the valence electronic structure of UN_2 is very similar to that of UO_2^{2+}, with the four expected MOs spanning an approximately equal eigenvalue range. Once again, the π MOs are more stable than the σ MOs, with the σ_u orbital being the highest occupied. The U−N bond is appreciably more covalent than the U−O bond in UO_2^{2+}, as evidenced by the much greater U/N overlap population and the more equal contribution of the uranium and nitrogen AOs to the MOs (shown in Figure 2 for the π orbitals only).

The bonding in UON^+ separates very nicely into U−O below U−N, with the π levels being once again more stable than the corresponding σ orbitals. Now, within the same molecule, it is clear that the U−N bonding is significantly more covalent than the U−O, and it may well be the greater covalency of the U−N bond that is responsible for the U−N distance being 0.092 Å shorter than the U−O. It is notable that the results of the present calculations on UON^+ are very similar to those from an analogous study on the isoelectronic UCO reported recently by Bursten et al.[36]

(ii) $UO(NPH_3)^{3+}$ and $U(NPH_3)_2^{4+}$. Having probed the valence electronic structures of UO_2^{2+} and the isoelectronic UON^+ and UN_2, I now turn to the mono- and bis(iminato) species $UO(NPH_3)^{3+}$ and $U(NPH_3)_2^{4+}$. At the risk of preempting the results of section B of this paper, I have assumed the U−N−P unit to be linear and have idealized the symmetry to the highest possible: i.e., C_{3v} for the mono iminato system and D_{3h} for $U(NPH_3)_2^{4+}$. Figure 3 presents an MO energy level diagram for these two systems constructed in the same way as Figure 2: i.e., with the eigenvalues of the HOMOs in both cases set arbitrarily to 0 eV and the boldface/italic/plain text coding as before. I shall now discuss the principal features of this

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(35) Heinemann, C.; Schwarz, H. *Chem. Eur. J.* **1995**, *1*, 7.
(36) Zhou, M.; Andrews, L.; Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1999**, *121*, 9712.

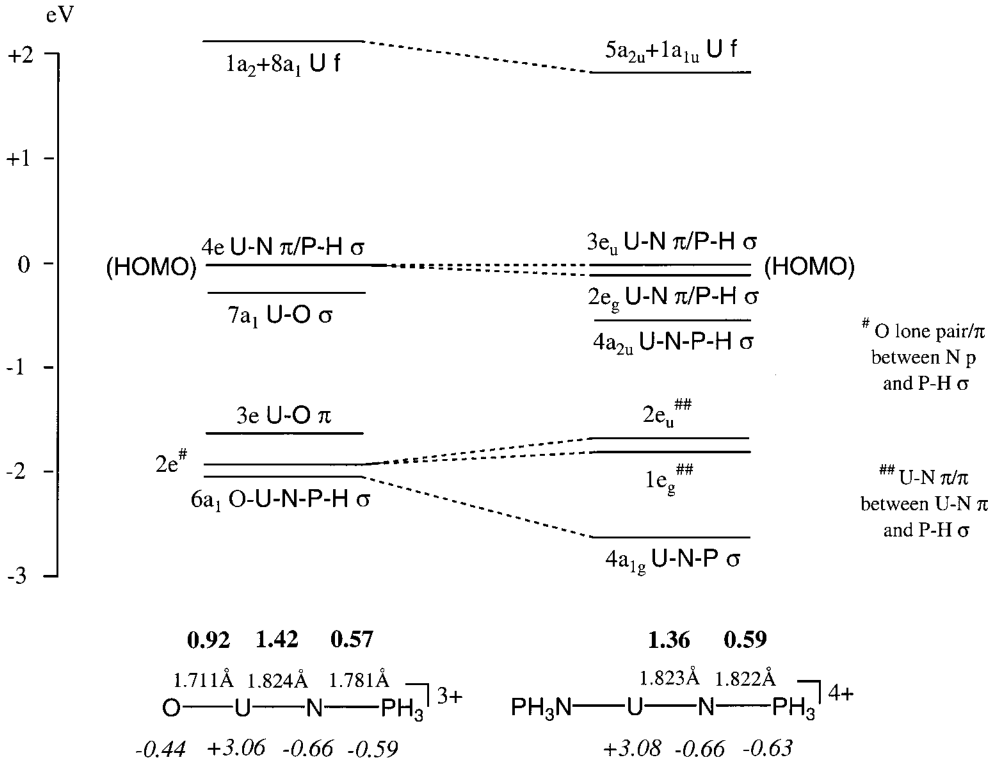

Figure 3. Valence molecular orbital energy level diagrams for $UO(NPH_3)^{3+}$ and $U(NPH_3)_2{}^{4+}$. The energy of the highest occupied molecular orbital has been arbitrarily set to 0 eV in all cases for comparative purposes. See the text for a description of the boldface/plain text/italic notation.

diagram in light of the preceding discussion of $UO_2{}^{2+}$, UON^+, and UN_2.

In both $UO(NPH_3)^{3+}$ and $U(NPH_3)_2{}^{4+}$ there are two valence MOs of uranium−ligand σ character and two of π symmetry, analogous to the species studied in section A(i). There are, however, additional MOs that are not present in $UO_2{}^{2+}$, UON^+, and UN_2, namely the 2e MO of $UO(NPH_3)^{3+}$ and the $1e_g$ and $2e_u$ levels of the bis(iminato) cation. As indicated on Figure 3, these orbitals have character different from that of any of the valence MOs of the triatomic systems. All feature P−H σ character combined in a bonding manner with nitrogen p ($UO(NPH_3)^{3+}$) or U−N π ($U(NPH_3)_2{}^{4+}$) to give an orbital of π symmetry with respect to the U−N axis. The 2e MO of $UO(NPH_3)^{3+}$ also features a nonbonding oxygen p_π contribution.

The U−O bonding in $UO(NPH_3)^{3+}$ is very similar to that in $UO_2{}^{2+}$. The bond length and Mulliken overlap populations are almost identical, the MO ordering is again π below σ (3e below $7a_1$), and the compositions of the U−O MOs are similar in the two cations ($UO(NPH_3)^{3+}$ MO composition data not shown). The U−N bond, however, is significantly different from that in UON^+ and UN_2. It is longer (by ca. 0.1 Å in comparison with UN_2 and nearly 0.2 Å in comparison with UON^+), an issue to which I return in section C, and the overlap population is smaller. Perhaps most notable, however, is the relative position of the U−N σ and π bonding levels ($6a_1$ and 4e, respectively), which has changed markedly from that in UON^+ and UN_2. In UON^+ the valence MO ordering is U−O π < U−O σ < U−N π < U−N σ, while in $UO(NPH_3)^{3+}$ the ordering is U−N σ < U−O π < U−O σ < U−N π; i.e., the U−N σ MO has moved from being the HOMO in UON^+ to the most stable of the valence levels in $UO(NPH_3)^{3+}$, and the U−N π MO is now the highest occupied orbital.

The U−N bonding in $U(NPH_3)_2{}^{4+}$ is similar to that in $UO(NPH_3)^{3+}$. The U−N bond length and overlap population are comparable to those in $UO(NPH_3)^{3+}$, and once again the U−N σ levels are more stable than the π levels. It is also notable that, as in the other centrosymmetric complexes $UO_2{}^{2+}$ and UN_2, the σ level of g symmetry ($4a_{1g}$) is more stable than that of u symmetry ($4a_{2u}$). Indeed, the σ_g/σ_u energy difference is appreciably larger in $U(NPH_3)_2{}^{4+}$ than in either $UO_2{}^{2+}$ or UN_2.

Two questions present themselves. First, why does the ordering of the U−N σ and U−N π MOs reverse from UON^+ and UN_2 to $UO(NPH_3)^{3+}$ and $U(NPH_3)_2{}^{4+}$? Second, is the reason for U−N σ_g below σ_u in $U(NPH_3)_2{}^{4+}$ the same as in $UO_2{}^{2+}$: i.e., is the pushing from below mechanism operative in the bis(iminato) system?

One possible factor in the answer to the first question is that π overlap is much more sensitive to bond length than σ overlap; i.e., the increased U−N distance in the iminato systems over the triatomic species may lead to reduced U−N π overlap and hence destabilize the U−N π bonding orbitals. To test this suggestion, I have generated a Walsh diagram for the elongation of the U−N distance in $UO(NPH_3)^{3+}$, and this is shown in Figure 4. In these calculations the atomic positions were fixed at their optimized values and the U−N distance was then varied from 1.70 to 1.86 Å in 0.02 Å steps. Figure 4 reveals that changing the U−N distance does indeed have a marked effect on the 4e (mainly U−N π bonding) orbitals, with a ca. 1 eV destabilization on going from r(U−N) = 1.70 Å to r(U−N) = 1.86 Å.

However, it is clear from Figure 4 that the destabilization of the 4e MOs is not responsible for the σ/π reversal, as the $6a_1$ U−N σ level is much more stable than the 4e level at all of the U−N distances calculated. A second factor is clearly at work, and one need look no further than the composition of the $6a_1$ MO to find it. At the optimized geometry this orbital is 15% U, 30% O, 28% N, 22% P, and 5% H in character, and a graphical visualization (not shown) indicates that it is σ bonding along the entire backbone of the molecule. The significant N−P σ (and, to a lesser extent, P−H σ) character of the $6a_1$ MO will

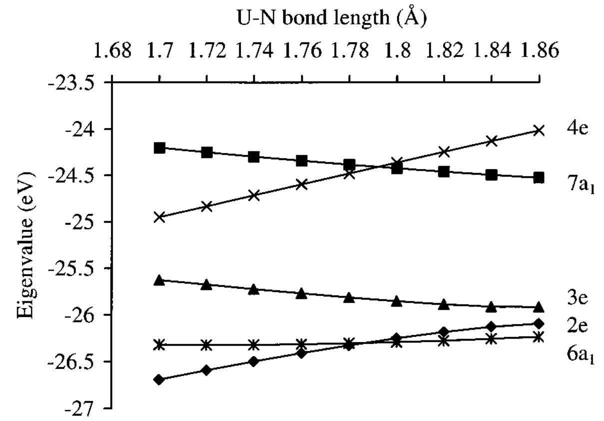

Figure 4. Walsh diagram for elongation of the U−N bond in $UO(NPH_3)^{3+}$.

naturally lower its eigenvalue from that of a purely metal−ligand σ orbital. Population analysis of the $4a_{1g}$ MO of $U(NPH_3)_2^{4+}$ reveals that it too is far from pure U−N σ in character, with a 34% P and 8% H contribution. I therefore suggest that σ bonding within the iminato ligands is responsible for the U−N σ/π MO ordering reversal in both $UO(NPH_3)^{3+}$ and $U(NPH_3)_2^{4+}$ with respect to UON^+ and UN_2. The destabilization of the U−N π levels with increasing U−N bond length contributes to the magnitude of the σ/π MO energy gap but does not of itself cause the reversal of the σ/π MO ordering.

An alternative way of thinking about the U−N σ stabilization in $UO(NPH_3)^{3+}$ is as follows. $UO(NPH_3)^{3+}$ can be regarded as being made up of a PH_3^{2+} unit bonded to UON^+. PH_3^{2+} is formally P(V) and may be considered to be PH_3 with its lone pair removed. As such, it is a good Lewis acid, and the bonding of PH_3^{2+} to the nitrogen atom of UON^+ therefore involves transfer of electron density from the nitrogen p_σ level to the PH_3^{2+} moiety. This process significantly perturbs the nitrogen p_σ level, dragging it down below all of the other valence MOs.

To establish if the pushing from below mechanism operates in the iminato systems, $U(NPH_3)_2^{4+}$ has been studied in a manner analogous to that shown for UO_2^{2+} in Figure 1: i.e., with the uranium 6p AOs placed in the frozen core and then freed up to play a role in the valence electronic structure (the results of the latter calculation are shown in Figure 3). All of the valence MOs remain essentially unperturbed by this process, with the exception of the $4a_{2u}$ (σ_u) orbital, which is significantly destabilized when the metal 6p AO is removed from the frozen core and which picks up a 6% uranium 6p contribution in the process. These results indicate that the pushing from below mechanism operates to destabilize the U−N σ_u MO of $U(NPH_3)_2^{4+}$ in a manner analogous to the U−O σ_u MO of UO_2^{2+}. Unlike UO_2^{2+}, however, the pushing from below mechanism is not the sole source of the σ_g/σ_u energy gap, which is significant even with the uranium 6p AO in the frozen core (the $4a_{2u}/4a_{1g}$ energy gap is 2.11 eV with the uranium 6p in valence (Figure 3) and 1.73 eV with uranium 6p in core). Once again, the MO compositions provide a clue to this energy difference, as the $4a_{1g}$ orbital has a significantly greater nitrogen, phosphorus, and hydrogen content than the $4a_{2u}$ orbital (45%, 34%, and 8%, respectively, vs 23%, 17%, and 2%). The bulk of the σ_g/σ_u energy gap in $U(NPH_3)_2^{4+}$ is therefore traced to the greater N−P and P−H σ character of the g symmetry orbital.

(iii) d vs f Orbital Covalency in UN_2, UO_2^{2+}, and $U(NPH_3)_2^{4+}$. The relative roles of the metal valence d and f functions in the bonding within actinide complexes continues to be of considerable interest. Table 2 presents the uranium AO contributions to the four valence MOs common to UN_2, UO_2^{2+}, and $U(NPH_3)_2^{4+}$: i.e., the π_g, π_u, σ_g, and σ_u orbitals. Perhaps the most striking feature of these data is the similarity between UO_2^{2+} and the bis(iminato) system. Indeed, although both $U(NPH_3)_2^{4+}$ and UN_2 have two nitrogen atoms coordinated to uranium, the metal contribution to the valence MOs in the former resembles that of UO_2^{2+} to a much greater extent than UN_2.

Table 2. Uranium Atomic Orbital Contributions (Mulliken Analyses) to the Valence Molecular Orbitals of UN_2, UO_2^{2+}, and $U(NPH_3)_2^{4+}$

	π_g	π_u	σ_g		σ_u	
UN_2	34% 6d	41% 5f	19% 6d	12% 7s	64% 5f	9% 6p
UO_2^{2+}	20% 6d	35% 5f	13% 6d	2% 7s	56% 5f	8% 6p
$U(NPH_3)_2^{4+}$	19% 6d	35% 5f	11% 6d		52% 5f	6% 6p

In all three molecules the uranium 6d AOs play a less important role than the 5f orbitals. From a comparison of the σ with the π MOs, it is clear that the 6d AOs are more important in π than σ, while the role of the 5f AOs is greater in the σ orbitals than the π. UN_2 differs from the other systems in that the relative d/f contribution to both the σ and π levels is greater; i.e., although the d content of the g symmetry MOs is less than the f contribution to the corresponding u levels, the d content as a fraction of the f is greater in UN_2 than in UO_2^{2+} and $U(NPH_3)_2^{4+}$. Put more simply, the role of the metal d AOs in the bonding in UN_2 is more significant than in UO_2^{2+} and $U(NPH_3)_2^{4+}$.

(iv) Is $U(NPH_3)_2^{4+}$ a Good Analogy for UO_2^{2+}? The present discussion is confined primarily to comparisons of the ground-state valence electronic structure of these systems. Within these boundaries it is difficult to state definitively whether the bis(iminato) system is analogous to the uranyl dication. Thus, although both molecules have four common uranium−ligand bonding MOs, the ordering of these orbitals is quite different between the two systems and the bis(iminato) ion has two additional valence levels. Furthermore, while the uranium AO contributions to the four common MOs are almost identical in UO_2^{2+} and $U(NPH_3)_2^{4+}$, implying approximately equal uranium−ligand covalency, the uranium−ligand overlap population is significantly greater in the bis(iminato) system. The pushing from below mechanism is seen to destabilize the σ_u MO of both systems to an approximately equal extent (with a concomitant uranium 6p AO contribution to this MO). In contrast, the optimized uranium−ligand bond length is appreciably shorter in UO_2^{2+} than in $U(NPH_3)_2^{4+}$.

In conclusion, I suggest that while it is certainly correct of Denning to describe uranium bis(iminato) complexes as *structural* analogues of the uranyl ion,[13,14] it is not clear that the analogy can be fully extended to the electronic structure. Nevertheless, similarities certainly do exist between the two systems, not the least of which is the formal metal/ligand bond order, discussion of which is presented in section C.

B. Linear or Bent? Probing the Effects of Bending at the Iminato Nitrogen. In the second part of this study I turn my attention from the electronic structure of "bare" iminato ions to the geometric structure of "real" iminato complexes: i.e., ones with equatorial ligands and larger R groups on the phosphorus atoms. Very few iminato complexes of uranium have been structurally characterized; one is the mono(iminato) anion $[UOCl_4\{NP(m\text{-}Tol)_3\}]^-$,[13] which features a nearly linear U−N−P unit with a UNP angle of 171.9°, almost identical with the 172° UNP angle found in $[U(C_5H_5)_3(NPPh_3)]$.[37] The question arises as to whether this near-linearity is a general feature of uranium

Table 3. Selected Metric Parameters from the Calculated Geometric Structure of $[UOCl_4\{NP(C_6H_5)_3\}]^-$ and the X-ray Crystal Structure of $[UOCl_4\{NP(m\text{-Tol})_3\}]^-$

complex	r(U−O)/Å	r(U−N)/Å	r(U−Cl)/Å	r(N−P)/Å	OUN angle/deg	UNP angle/deg
$[UOCl_4\{NP(m\text{-Tol})_3\}]^-$ [13]	1.759	1.901	2.620, 2.635, 2.634, 2.636	1.633	179.0	171.9
$[UOCl_4\{NP(C_6H_5)_3\}]^-$	1.796	1.986	2.636, 2.648, 2.636, 2.632	1.597	178.6	175.3

iminato complexes and if so, why. In this section I report the results of calculations on three uranium iminato systems with different R groups, the bis(iminato) species $[UCl_4\{NPR_3\}_2]$ (R = H, Me) and the mono(iminato) $[UOCl_4\{NP(C_6H_5)_3\}]^-$, which is very closely related to the structurally characterized toluene system. The aim of the study is to establish the most favored UNP angle and, through the energy decomposition scheme implemented in ADF (see part B in Computational and Theoretical Details) to determine whether the angular preference is driven by electronic and/or steric factors.

The process adopted was in all cases as follows. First, the geometry of the molecule was optimized within the constraint of C_{2h} symmetry for the bis(iminato) systems and C_s for the mono(iminato) anion. Second, a series of single-point calculations was performed in which all of the atoms were initially placed at their optimized geometry and one UNP angle was subsequently reduced from 180° in 10° steps to as small an angle as would allow SCF convergence. These distortions were chosen so as to maximize the distances between the R groups and the chlorine atoms: e.g., moving the PR_3 unit away from chlorine atoms which, in the optimized geometries, eclipse an R group. Finally, the total bonding energy was calculated for each UNP angle and broken down into electronic and steric components. I note that this approach is likely to produce an upper bound to the dependence of total bonding energy on UNP angle because no geometric relaxation is allowed as the angle is varied.

Before examination of the results of these distortions, it is worth taking a moment to compare the calculated geometry of $[UOCl_4\{NP(C_6H_5)_3\}]^-$ with the X-ray crystal structure of $[UOCl_4\{NP(m\text{-Tol})_3\}]^-$. Selected metric parameters are collected in Table 3, from which it may be seen that there is generally good agreement between theory and experiment (particularly given the size of the molecule in question) with the possible exception of the U−N distance, which is overestimated in the calculation by 0.085 Å. Comparison of the U−N distance in $[UOCl_4\{NP(C_6H_5)_3\}]^-$ with that calculated for $UO(NPH_3)^{3+}$ (Figure 3) reveals a 0.16 Å lengthening on coordination of the equatorial chlorine atoms, indicating a significant weakening of the U−N bond by this process.

The absolute values of the total molecular bonding energy (and its breakdown into steric and electronic components) will, of course, be very different in the three systems studied. To better facilitate comparison, I have assigned each molecule a total bonding energy of 0 kJ/mol at a UNP angle of 180° and calculated the energy at other angles relative to that zero. The results of this process are shown in Figure 5.

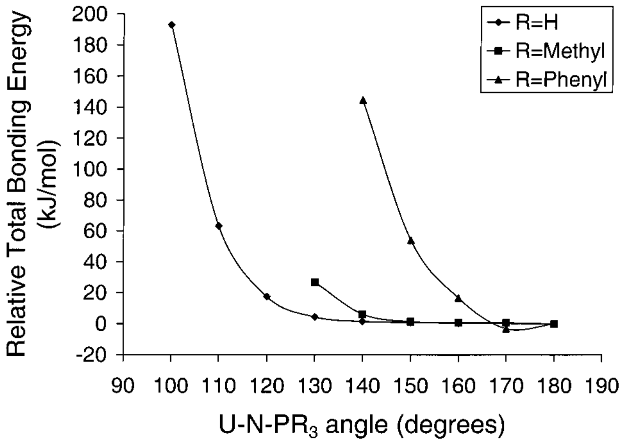

Figure 5. Dependence of the total molecular bonding energy on UNP angle for $[UCl_4\{NPR_3\}_2]$ (R = H, Me) and $[UOCl_4\{NP(C_6H_5)_3\}]^-$. Each complex is arbitrarily assigned a total bonding energy of 0 kJ/mol at a UNP angle of 180° for comparative purposes.

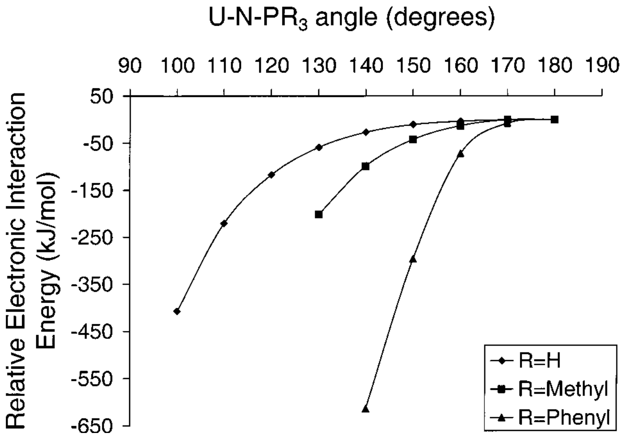

Figure 6. Dependence of the electronic interaction energy on UNP angle for $[UCl_4\{NPR_3\}_2]$ (R = H, Me) and $[UOCl_4\{NP(C_6H_5)_3\}]^-$. Each complex is arbitrarily assigned an electronic interaction energy of 0 kJ/mol at a UNP angle of 180° for comparative purposes.

The data obtained for the PH_3 system indicate that the potential energy surface for bending at the nitrogen atom is essentially flat between UNP angles of 180 and 120°. There is a very small preference for linearity, but this is on the order of a few kJ/mol. Only when the UNP angle becomes very acute (110° or less) does the total energy begin to attain appreciably less stable values. A similar situation exists for the PMe_3 system, although the width of the potential well is narrower, the first significant rise in energy coming at a UNP angle of 130°. Unfortunately, it proved impossible to achieve SCF convergence on this molecule for geometries in which the UNP angle was less than 130°, but the trend shown in Figure 5 is clear enough.

The data for the triphenyl anion are somewhat different from those obtained for the bis(iminato) complexes. First, the lowest energy is now not at exactly 180° but at 170°, and second, the width of the potential well is much less; e.g., a distortion of only 30° from linearity produces a destabilization of ca. 50 kJ/mol. These results are certainly in agreement with the experimental observation of near-linearity in $[UOCl_4\{NP(m\text{-Tol})_3\}]^-$ and suggest that this is due to intra- rather than intermolecular effects.

To probe further the nature of these intramolecular effects, I have broken down the total bonding energy into its electronic and steric components. Figure 6 plots the electronic interaction energy as a function of the UNP angle, with an arbitrary value of 0 kJ/mol assigned to each complex at a UNP angle of 180°. It is clear that in all cases there is an electronic preference for bending at the nitrogen atom and that this preference increases

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(37) Cramer, R. E.; Edelmann, F.; Mori, A. L.; Roth, S.; Gilje, J. W.; Tatsumi, K.; Nakamura, A. *Organometallics* **1988**, *7*, 841.

Table 4. Bonding Characteristics of Selected Valence Molecular Orbitals of [$UCl_4\{NPH_3\}_2$] at UNP Angles of 180 and 100°

molecular orbital	stabilization (kJ/mol)	character at 180°	character at 100°
14a′	87.8	U−N σ bonding	U−N σ bonding, U−P σ bonding
15a′	87.8	Cl p_σ nonbonding	Cl p_σ nonbonding, U−Cl σ bonding
5a″	60.8	mainly Cl p_π and N p_π nonbonding with some U−Cl and U−N π bonding	as at 180° plus increased U−N π bonding
19a′	54.0	mainly U−Cl π bonding with some U−Cl σ bonding and U−N π bonding	as at 180° without the U−N π bonding
18a′	49.2	U−Cl σ bonding, U−N π bonding	U−Cl σ bonding, U−N π bonding, U−N σ bonding

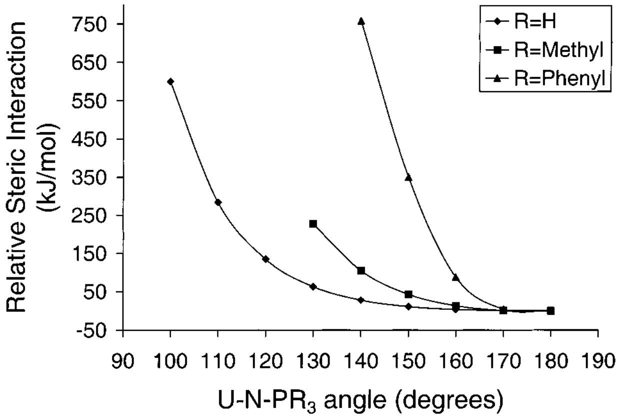

Figure 7. Dependence of the steric interaction energy on UNP angle for [$UCl_4\{NPR_3\}_2$] (R = H, Me) and [$UOCl_4\{NP(C_6H_5)_3\}$]$^-$. Each complex is arbitrarily assigned a steric interaction energy of 0 kJ/mol at a UNP angle of 180° for comparative purposes.

in the order R = H < R = Me < R = Ph; i.e., the electronic interaction energy becomes more favorable most rapidly for the mono(iminato) anion.

Although Kohn and Sham's purpose in introducing orbitals into density functional theory was to facilitate calculation of the kinetic energy of a system of noninteracting electrons,[5] a beneficial side effect is to make the analysis of density functional theory calculations more accessible to chemists. Thus, notwithstanding the fact that the electronic interaction energy is not merely the sum of the one-electron energies, some insight into the origin of the trends shown in Figure 6 may be gained by consideration of the variation in the energies and compositions of the one-electron MOs as the UNP angle is reduced. This is now discussed for [$UCl_4\{NPH_3\}_2$], analysis of which reveals that there are five valence MOs which are stabilized by more than 0.5 eV (≡48.2 kJ/mol).[38] The bonding characteristics of these MOs are collected in Table 4 (note that the orbitals carry C_s symmetry labels, as this is the highest possible molecular symmetry when the UNP angle is reduced from 180°), from which it may be seen that the reason for the stabilization is in most cases the acquisition of enhanced bonding character as the UNP angle is reduced. Thus, although essentially qualitative, this analysis does provide some rationalization of the increased electronic interaction energy of [$UCl_4\{NPH_3\}_2$] as the UNP angle is reduced.

Given that all three molecules have an electronic preference for bending at the nitrogen atom, it is no surprise that the overall preference for linearity is driven by the steric interaction energy. This is shown in Figure 7, from which it may be seen that bending away from a UNP angle of 180° results in all cases in an increase in steric repulsion (i.e., the steric interaction energy becomes more positive). This increase in steric repulsion is most rapid for R = Ph and subsequently decreases in the order R = Me > R = H.

We may therefore conclude that all three iminato complexes display a preference for linearity (or near-linearity) at the nitrogen atom, and that this preference decreases in the order R = Ph > R = Me > R = H. The driving force for this linear preference is steric, which overcomes an electronic preference for smaller UNP angles. It would be of great interest to establish experimentally the angle at nitrogen in uranium iminato complexes with R groups on the phosphorus atom smaller than the toluene case reported by Brown and Denning[13] or the phenyl example of Cramer et al.[37] The prediction from the present study is that uranium iminato complexes with less bulky PR_3 units may well be significantly bent at nitrogen, as the intramolecular driving force to linearity is so small at angles above ca. 130° that intermolecular factors such as crystal packing forces may well determine the UNP angle.

C. Comparison of the Structure and Bonding in the Title Iminato Complexes with d Block Imido Systems. The electronic structure and bonding of transition metal imido compounds is an area of continuing interest. One of the structural features that chemists often consider is the linearity (or otherwise) of the M═N−R linkage and the electronic consequences or significance of any deviations from linearity. The electronic and geometric structures of d block imido compounds have recently been nicely reviewed by Cundari,[39] and much of the discussion presented in this review is relevant to the present work. Cundari notes that Rankin et al.[40] used the extended Hückel (EH) approach to conclude that the potential surface for imido bending in [$OsO_2(NR)_2$] (R = Me, ^{t}Bu) is essentially flat. Jørgensen[41] has employed the same method to study [$TaH(C_5H_5)_2NR$] (R = Me, Ph; a model for the structurally characterized [$TaH(C_5Me_5)_2NPh$][42]) and found that, when R is aliphatic, there is little, if any, preference for the linear over the bent structure. In contrast, replacement of Me by Ph produces a pronounced preference for linearity at the imido nitrogen atom, which is traced to the fact that bending makes the HOMO much less stable (and decreases the N−C(ipso) overlap population) by increasing the N−C(ipso) π* character of this orbital. This neatly rationalizes the linearity observed experimentally in [$TaH(C_5Me_5)_2NPh$].[42]

Previous EHMO calculations therefore indicate that, provided the group attached to nitrogen is bound in a σ-only manner, bending at the imido nitrogen is a facile process, and NMR

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[38] Note that there are many more than five MOs which are stabilized by <0.5 eV and several that are destabilized by the bending. These are not discussed, as my aim is not to account for the behavior of all of the MOs throughout the distortion but to provide some rationalization for the trends shown in Figure 6.

[39] Cundari, T. R. *Chem. Rev.* **2000**, *100*, 807.

[40] Rankin, D. W. H.; Robinson, H. E.; Danopoulos, A. A.; Lyne, P.; Mingos, D. M. P.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1994**, 1563.

[41] Jørgensen, K. A. *Inorg. Chem.* **1993**, *32*, 1521.

[42] Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, L.; Nua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82.

studies by Bradley et al.[43] support this conclusion. The present, more sophisticated, calculations agree very much with the previous d block work, indicating that for small PR_3 groups the potential surface for bending at iminato nitrogen is also very flat. Further d/f block comparisons will hopefully result from work in progress to bring the methodology behind the analysis in section B to bear on the pseudo-octahedral d^0 titanium imido compounds of Mountford et al.[44−46]

One of the key issues in d block imido chemistry that is not a factor in uranium compounds is the 18-electron rule. Thus, the rationalization of the bonding in $[TaH(C_5Me_5)_2NPh]$[39,42] involves only a double bond between the metal and the nitrogen in order to avoid the 20-electron count implied by a Ta−N triple bond. Perhaps the classic example in this area is the Os(N-2,6-C_6H_3-*i*-$Pr_2)_3$ system of Schrock et al.[47] Linearity at the nitrogen atoms implies formal triple bonds and a 20-electron count at the metal center. However, electronic supersaturation of the metal is avoided because two of these electrons occupy a nitrogen-localized nonbonding MO,[48] and the Os−N bond order may be formally regarded as 2.67. Moving to the f block circumvents the 18-electron rule, and one has greater flexibility when it comes to electron counting. On the basis of the near-linearity of the UNP unit and the shortness of the U−N bond, Brown and Denning conclude that the formal U−N bond order in their iminato compounds is 3.[13,14] This means that all of the valence electrons of the nitrogen atoms are involved in U−N bonding, producing a 20-electron count for $[UCl_4\{NPR_3\}_2]$. There is nothing in the present calculations to suggest that this analysis is erroneous. Certainly there are no MOs in any of the bare iminato ions or chloro complexes that have predominant nitrogen p_π lone pair character, as would be required for formal U−N double bonds. Having said that, it is noticeable that the U−N bond length in the bare iminato ions and especially the chloro complexes are significantly longer than those in UON^+ and UN_2. Given that the U−N bond order in these latter systems is certainly 3, one might argue that it is somewhat less than 3 in the iminato complexes on the grounds of longer U−N distances. On balance, however, I favor the description of the U−N bond in the iminato systems as a triple bond, as indeed is the U−O bond in the uranyl dication.

Conclusions

The electronic and geometric structures of eight uranium compounds have been addressed using computational methods based on Kohn−Sham density functional theory. A number of conclusions can be drawn from these studies, and these are set out below.

1. The valence MO ordering of UO_2^{2+} is confirmed as that put forward by Denning:[7] i.e., $\pi_g < \pi_u < \sigma_g \ll \sigma_u$ (HOMO). The significant energy gap between the σ_g and σ_u orbitals is traced to the so-called "pushing from below" mechanism: a filled−filled interaction between the semi-core uranium 6p AOs and the σ_u valence level.

2. The U−N bonding in UON^+ and UN_2 is significantly more covalent than the U−O bonding in UON^+ and UO_2^{2+}.

3. $UO(NPH_3)^{3+}$ and $U(NPH_3)_2^{4+}$ are similar to UO_2^{2+}, UON^+, and UN_2 in that they possess two valence MOs of metal−ligand σ character and two of π character, although they have additional valence MOs not present in the triatomic systems. The ordering of the U−N valence MOs is different in the iminato systems, with the U−N σ levels now more stable than the U−N π orbitals. This is traced to significant N−P (and P−H) σ character in the U−N σ levels. The pushing from below mechanism is found to destabilize the U−N f_σ MO with respect to the U−N d_σ level in $U(NPH_3)_2^{4+}$. The U−N bond lengths in the iminato ions are longer than in UON^+ and UN_2.

4. The uranium f AOs play a greater role in metal−ligand bonding in UO_2^{2+}, UN_2 and $U(NPH_3)_2^{4+}$ than do the d AOs. However, while the relative roles of the uranium d and f AOs are similar in UO_2^{2+} and $U(NPH_3)_2^{4+}$, the metal d AOs have a more important role in the bonding in UN_2.

5. The preferred UNP angle in $[UCl_4\{NPR_3\}_2]$ (R = H, Me) and $[UOCl_4\{NP(C_6H_5)_3\}]^-$ is found to be close to 180° in all cases. This preference for linearity decreases in the order R = Ph > R = Me > R = H (i.e., the width of the essentially flat part of the potential well is greatest for R = H and least for R = Ph) and is traced to steric effects which in all cases overcome an electronic preference for bending at the nitrogen atom.

6. Comparison of the present calculations with previous extended Hückel work on d block imido systems reveals that there is little or no preference for linearity over bending at the nitrogen when R is (a) only σ bound to the nitrogen and (b) sterically unhindered.

7. The U/N bond order in iminato complexes is best described as 3.

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(43) Bradley, D. C.; Hodge, S. R.; Runnacles, J. D.; Hughes, M.; Mason, J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1992**, 1663.

(44) Collier, P. E.; Dunn, S. C.; Mountford, P.; Shishkin, O. V.; Swallow, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3743.

(45) Blake, A. J.; Collier, P. E.; Dunn, S. C.; Li, W.-S.; Mountford, P.; Shishkin, O. V. *J. Chem. Soc., Dalton Trans.* **1997**, 1549.

(46) Kaltsoyannis, N.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1999**, 781.

(47) Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642.

(48) Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595.