Table II. Relative Heats of Formation of Tertiary Alkyl Ions

Ion	kcal/mol		
	This work	Ref 9a	Ref 9b
$(CH_3)_3C^+$ [a]	0	0	0
$(CH_3)_2C^+C_2H_5$ [b]	-6.8 ± 0.2	-7.6 ± 0.2	-8.0 ± 0.2
$(CH_3)_2C^+CH_2CH_2CH_3$ [b]	-13.3 ± 0.4	-14.1 ± 0.4	-13.5 ± 0.4

[a] On the basis of the appearance potential of t-$C_4H_9^+$ from neopentane (B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34,** 189 (1961)), a value of 168.2 ± 0.55 kcal/mol can be derived for $\Delta H_f(t\text{-}C_4H_9^+)$ (taking a value of 34.8 ± 0.2 kcal/mol for $\Delta H_f(CH_3)$ (K. E. McCulloh and V. H. Dibeler, *ibid*, **64,** 4445 (1976)). The value for $\Delta H_f(t\text{-}C_4H_9^+)$ is commonly based on the heat of formation and the ionization potential of the t-C_4H_9 radical. Taking the revised value for $\Delta H_f(t\text{-}C_4H_9)$ (12 ± 1 kcal/mol) (W. Tsang, *Int. J. Chem. Kinet.*, in press) and the ionization potential reported earlier (F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48,** 955 (1970)) (159.8 ± 1 kcal/mol), one obtains $\Delta H_f(t\text{-}C_4H_9^+) = 172 \pm 2$ kcal/mol, rather than the unrevised number of 169.1 kcal/mol usually quoted. [b] Error limits are essentially those ascribed to the heats of formation of the relevant neutral species.

$(\Delta S_{\mathrm{Rot}} + \Delta S_{\mathrm{Int}})$ would be -1.8 cal/(K mol) if the symmetry numbers associated with acetone and protonated acetone were, respectively, 2 and 1.

Accepting that there is no ΔS_{Rot} associated with the protonation of acetone, a re-examination of the results for equilibrium 1 (Table I) reveals that since ΔS_{Rot} (eq II) is now be assumed to be $R \ln {}^6\!/_2$ or 2.19 cal/(K mol),[6] and ΔS_{Int} is 1.14 cal/(K mol), the measured entropy change of 0 can only be accounted for if there is an additional unexplained component of the entropy change equal to -3.3 cal/(K mol). This entropy change can best be explained in terms of the loss of an internal rotation when a C–C bond in t-$C_4H_9^+$ is replaced by a double bond in isobutene.[7] An alternate view may be taken that the experimental result simply indicates that there is substantial rotational-vibrational coupling in the *tert*-butyl ion which invalidates the calculation of ΔS_{Rot} using such simplified concepts as symmetry numbers or losses of internal rotations. Taking a value of 70.17 cal/(K mol) for the absolute entropy of isobutene,[8] these results indicate that the absolute entropy of the *tert*-butyl ion must be (70.17 + 1.14) cal/(K mol) or 71.3 cal/(K mol) (again taking the entropy change associated with the protonation of acetone to be 0).

Figure 1 also shows van't Hoff plots determined for the equilibria

$$(CH_3)_2CCH_2CH_3^+ + CH_3COCH_3 \rightleftarrows (CH_3)_2C{=}CHCH_3 + (CH_3COCH_3)H^+ \quad (3)$$

and

$$(CH_3)_2{}^+CCH_2CH_3 + CH_3COOCH_3 \rightleftarrows (CH_3)_2C{=}CHCH_2CH_3 + (CH_3COOCH_3)H^+ \quad (4)$$

The results are summarized in Table I. Since, in both cases, there should be no net change in external rotational symmetry numbers, it is only necessary to take into account ΔS_{Int} in order to calculate from the observed entropy changes the ΔS which may be associated with changes in internal rotation. These results lead to the conclusion that the loss of internal rotation in going from a C_5 or C_6 tertiary carbonium ion to the corresponding 2 olefin corresponds to an entropy change of -1.4 to -1.8 cal/(K mol).[9] Taking a value of 80.92 cal/(K mol) for the absolute entropy of 2-methyl-2-butene, these results lead to a value of 82.3 cal/(K mol) for the absolute entropy of the *tert*-pentyl ion.

From these results, relative heats of formation of the $(CH_3)_3C^+$, $(CH_3)_2C^+C_2H_5$, and $(CH_3)_2C^+CH_2CH_2CH_3$ ions were derived, and are compared in Table II with relative heats of formation of these ions derived from equilibrium constants for hydride-transfer equilibria.[10] The agreement is good within the error limits stated.

Acknowledgment. The authors express their appreciation to Dr. Michael Henchman for his thoughtful comments.

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N-Cycloheptatrienylidenemethylamine Oxide: Synthesis, Electronic Spectra, and Cycloadditions of a Fulvenoid Dipole

Sir:

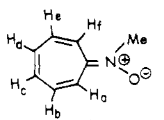
The union of one terminus of a 1,3 dipole with both termini of a polyene gives a "fulvenoid dipole". Whether such a compound is stabilized or destabilized with respect to the fragments depends on the symmetries and relative energies of the π orbitals of the isolated moieties. Using the symbol X for the 1,3-dipole fragment,[1] the stabilities and reactivities of various fulvenoid dipoles can be predicted according to the simple model given in Figure 1.

Because of the polyene HOMO and LUMO symmetries, X will stabilize the diene if X is a good donor, while it will stabilize the triene only if X is a good acceptor. In such cases, strong HOMO–LUMO interactions between the fragments will stabilize the composite system and decrease its reactivity. However, union of a good donor, X, with the triene will lead not to stabilization, but to four-electron destabilization owing to closed-shell repulsion. Furthermore, the resulting increase in triene HOMO energy will lead to increased reactivity toward electrophiles. Union of a good acceptor X with a diene leads neither to stabilization nor to destabilization, but the diene

LUMO is lowered, enhancing its reactivity toward nucleophiles. The model rationalizes why union of diazomethane—a good donor (IP = 9.0 eV)[2] and poor acceptor (EA ≈ −1.8 eV)[2]—leads to the stabilized diazocyclopentadiene[3] upon union with a diene, and gives the highly reactive destabilized diazocycloheptatriene upon union with a triene.[4]

The model also predicts that union of the nitrone (CH_2=$^+$NH—O^-) carbon to a diene will produce a highly reactive system resembling cyclopentadienone, but union with a triene will give a stabilized system, resembling tropone. This results because the nitrone is only a moderate donor (IP = 9.7 eV), but a good acceptor (EA = 0.5 eV).[2] In confirmation of these predictions, we wish to report here the preparation of *N*-cycloheptatrienylidenemethylamine (**1**), the unusual physical properties of this species, and its varied cycloaddition behavior, which gives further insight into the phenomenon of periselectivity.[6]

Addition of methyl iodide to a solution of tropone oxime in methanol in the presence of excess sodium methoxide gave a mixture of *O*-methyl tropone oxime and *N*-methylcycloheptatrienylidene nitrone (**1**) in an isolated ratio of 1:1. Pure **1** was obtained in 20% yield by chromatography on Florisil.



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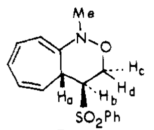

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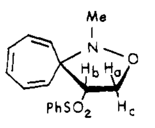

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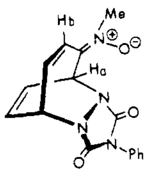

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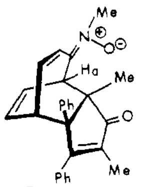

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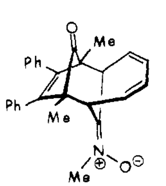

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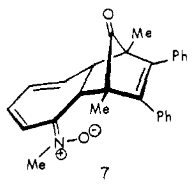

7

Compound **1** is a coffee-brown oil which has an *N*-methyl singlet at δ 3.68 and a complex multiplet at 6–6.5 ppm (5 H) in the NMR spectrum ($CDCl_3$).[7] A broad doublet at δ ~7.2 is assigned to H_a, which lies in the nitrone deshielding zone near oxygen. This proton is dramatically shifted to lower field by $Eu(fod)_3$ and becomes a distinct doublet of doublets (J_{ab} = 12 Hz, J_{af} = 2 Hz). Both H_b (J_{ab} = 12 Hz, J_{bc} = 7.5 Hz) and H_c (J_{cd} = 12 Hz, J_{bc} = 7.5 Hz) are also resolved under these conditions. Because the chemical shifts of **1** resemble those of the planar tropone molecule,[8] and are distinctly different from those of the puckered cycloheptatriene molecule,[9] **1** appears to be substantially stabilized and planar. **1** shows considerably chemical stability, slowly decomposing ($t_{1/2}$ ~ 1 week) in concentrated solution at 80 °C.

The ultraviolet spectrum of **1** is substantially red shifted compared with those of other nitrones or of tropone. In 95% EtOH, **1** has three distinct maxima at 342 nm (ε 13 000), 250 (9500) and 210 (10 400). The long wavelength band tails to 440 nm, leading to the coloration of the compound. The isomeric *C*-phenyl-*N*-methyl nitrone has absorptions at 290 nm (ε 21 200) ($\pi\pi^*$), 223 (8700) ($n\pi^*$), and 207 (9500) ($\pi\pi^*$) in ethanol.[10]

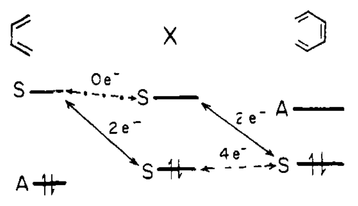

Figure 1. Frontier orbital interactions ensuing upon union of a fragment, X, across the termini of a diene or triene.

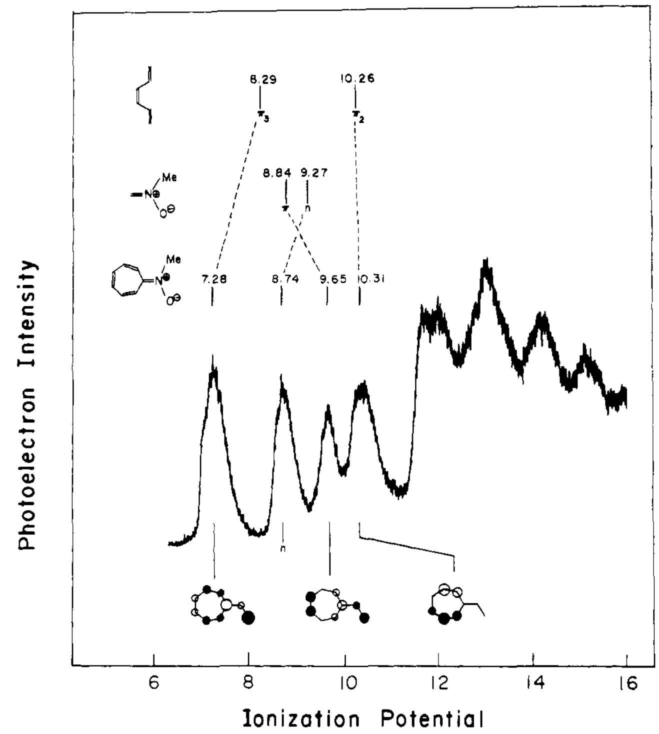

Figure 2. Ionization potentials of hexatriene, *N*-methyl nitrone, and **1**. The MOs of **1** (STO-3G) are shown under the corresponding ionization bands in the photoelectron spectrum of **1**.

The photoelectron spectrum of **1**, shown in Figure 2, indicates that **1** has substantially lower IPs than are observed for similar nitrones. Figure 2 compares the ionization potentials of **1** with those of hexatriene[11] and those estimated for *N*-methyl nitrone.[12] Because of the symmetries and energies of the triene π MOs, there can be strong interactions between the triene HOMO and the nitrone π HOMO, but the triene SHOMO should be essentially unaltered. The first IP of **1** is 7.28 eV, 0.8 eV lower than that of *C*-phenyl-*N*-methyl nitrone.[12] This low IP causes the substantial bathochromic shift of the first UV absorptions and should cause enhanced electron-donor and nucleophilic behavior of **1** compared with other nitrones.

In fact, only cycloadditions to electron-deficient dipolarophiles proceeded at reasonable rates.[13] Reaction of **1** with phenyl vinyl sulfone in chloroform at 70 °C for 2 days gave, after chromatography, a crystalline 1:1 adduct, **2**,[14] mp 159–160 °C dec, in 45% yield. The structure of this adduct was determined by NMR studies of **2** and the monodeutero derivative resulting from exchange of H_b for deuterium with NaOD/D_2O/THF. H_b is coupled to H_a by only 1 Hz,[14] implying trans arrangement of H_a and H_b.

The formation of **2** was unexpected, since it is formally a [10 + 2] cycloaddition adduct, thermally forbidden if it is formed in a concerted suprafacial fashion. However, when the reaction was followed by NMR, a new adduct **3**, was found to be the initial product of the reaction. Compound **3** could not be isolated in a pure state, since it rearranges to **2** at a rate comparable with its rate of formation. **3** has an *N*-methyl singlet at δ 2.33 and a resolved pattern indicating the presence of the 4-phenylsulfonylisoxazolidine.[14] In $CDCl_3$ or benzene-d_6 at 70 °C, **3** rearranges to **2** with a half-life of 1 day, while, in CD_3OD, the rearrangement is complete in 1 h. On attempted silica gel chromatography of **3**, only **2** was obtained. Combined with the observation that **3** is formed more slowly in polar solvents than in nonpolar, this indicates that **3** is formed by a concerted 1,3-dipolar cycloaddition, while **2** is subsequently formed by a stepwise 1,7-sigmatropic shift involving a zwitterionic intermediate.

By contrast to the electron-deficient sulfone, *N*-phenyltriazolinedione (PTAD) reacts at −10 °C as a dienophile with the triene unit of **1** to give the Diels–Alder adduct, **4**, mp 167–168 °C dec, in 44% yield. The NMR spectrum of this compound shows a nitrone *N*-methyl singlet at δ 3.78 and remaining coupling patterns similar to those of the tropone–PTAD adduct.[15] The only major difference is the very low-field resonance of the tertiary bridgehead proton, H_a, which appears at δ 6.86, downfield by 1.3 ppm from the resonance of the analogous proton in the tropone adduct.[15] H_a is held rigidly in the plane of the nitrone, as is H_b, which has been shifted downfield by 0.4 ppm in **4** as compared to its position in the tropone–PTAD adduct. Because of the dramatic downfield shift of H_a, we assign the nitrone configuration as that shown in the drawing. Similar large downfield shifts are observed for hydrogens syn to, and in the plane of, the oxygen of electronically similar nitrosamines.[16]

The reaction of **1** with 2,5-dimethyl-3,4-diphenylcyclopentadienone in benzene at 80 °C for 40 h gives a major adduct, **5**, mp 198–200 °C dec, in 43% yield, and a minor adduct, **6**, mp 155–156 °C dec. The adduct, **5**, has an α,β-unsaturated ketone absorption at 5.96 μ in the IR and methyl resonances for methyl at saturated and unsaturated carbons at δ 1.01 and 1.78, respectively. These data indicate that **1** added to a 2,3 double bond of the cyclopentadienone. The nitrone *N*-methyl resonance at δ 3.77 indicates the retention of the nitrone moiety, and the remainder of NMR spectrum indicates that the carbon skeleton of **5** was identical with that of the analogous adducts of tropone[17] or cycloheptatriene[18] with the same cyclopentadienone. Once again, H_a in **5** is shifted downfield by 1.5 ppm from its position in the analogous tropone adduct,[17] indicating that the nitrone oxygen is syn to H_a. The analogous adducts of tropone and cycloheptatriene with this cyclopentadienone have been shown to arise by Cope rearrangements of primary [4 + 2] adducts,[17,18] and, by analogy, we suggest that **5** is formed from the unobserved [4 + 2] adduct, **7**.

The minor adduct, **6**, mp 155–156 °C dec, proved to be a [6 + 4] adduct. The carbonyl stretch at 5.69 μ in **6** is closer to that of the [6 + 4] adducts of the same cyclopentadienone with cycloheptatriene (5.71 μ) and with tropone (5.68 μ) than it is to that of the [4 + 2] adduct with cycloheptatriene (5.66 μ). Less equivocally, the bridgehead protons each appear as doublets of doublets at δ 3.89 and 5.23, coupled to each other by 4 Hz, and to vicinal protons by 6.8 Hz. The alternative structure, **7**, is incompatible with these data.

In both **4** and **5**, the nitrone oxygen is syn to the bridgehead, most probably in the sterically least hindered configuration. Since *C*-aryl-*N*-alkyl nitrones have barriers to CN rotation of 32-35 kcal/mol[19] (e.g., (*E*)-*C*-phenyl-*N*-*tert*-butyl nitrone isomerizes to the *Z* isomer in 24 h at room temperature),[20] it is likely that the configurations of **4** and **5** do not necessarily represent the configuration of the initially formed cycloadduct. The nitrone moieties in **4** and **5** are effectively shielded from external attack, and we have been unable either to hydrolyze, or to react alkenes with, the nitrone group.

The different periselectivities found in the three reactions are quite startling. The regiospecific formation of **3** is unusual, since most nitrones give mixtures of 4- and 5-arylsulfonylisoxazolidines with phenylvinyl sulfone.[6] However, the cycloheptatrienylidene substituent serves as a powerful donor, lowering the nitrone IP, and increasing the nitrone oxygen nucleophilicity relative to carbon, thus giving only the "reversed" 4-substituted isoxazolidine.[21]

In spite of the high concentration of HOMO electron density at the nitrone oxygen, O–N overlap is proportionally smaller than C–N overlap at a given distance.[22] This, and repulsion of the partially negative N and O atoms in PTAD and **1**, respectively, diverts the cycloaddition to the normal Diels–Alder type.

Finally, the cycloaddition of the cyclopentadienone to **1** occurs in the modes analogous to those observed with cycloheptatriene and tropone. The lack of formation of a potential [10 + 4] adduct must arise from the relatively large mismatch in distances between the termini of the diene and those of formal 1,9 dipole.

The ability of the cycloheptatrienylidene moiety to stabilize electron-deficient 1,3 dipoles, and of the cyclopentadienylidene moiety to stabilize electron-rich dipoles, is being investigated as a means to gain entry to isolable derivatives of 1,3 dipoles of otherwise fleeting existence.

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(14) **2**: H_b, δ 4.21 (J_{ab} = 1 Hz, J_{bc} = 9.1 Hz, J_{bd} = 3.8 Hz); H_a, δ 2.47; H_c, δ 4.34 H_d, δ 4.88. **3**: H_a, δ 4.06 (J_{ab} = 8.5 Hz, J_{ac} = 10.7 Hz); H_b, δ 4.32 (J_{ba} = 8.5 Hz, J_{bc} = 4.0 Hz); H_c, δ 4.68 (J_{ca} = 10.7 Hz, J_{cb} = 4.0 Hz).

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Preparation and Properties of the Actinide Borohydrides: $Pa(BH_4)_4$, $Np(BH_4)_4$, and $Pu(BH_4)_4$[1]

Sir:

Uranium(IV) borohydride, a volatile dark green solid, was first synthesized during the Manhattan Project.[2a] Hoekstra and Katz[2b] reported the preparation of the much less volatile, but isostructural, $Th(BH_4)_4$ in 1949. Recently uranium borohydride[3,4] and its etherate complexes[5] have again been the subject of structural and spectroscopic investigations. As part of our program on the properties of actinide borohydrides, we report in this communication the synthesis of $Pa(BH_4)_4$, and the first successful syntheses of $Np(BH_4)_4$ and $Pu(BH_4)_4$, the remaining borohydride complexes of the first five elements of the actinide series, and some of their physical properties.[6]

All five actinide compounds, $An(BH_4)_4$, are made by the solvent-free reaction of the anhydrous tetrafluoride with $Al(BH_4)_3$, viz.

$$AnF_4 + 2Al(BH_4)_3 \rightarrow An(BH_4)_4 + 2AlF_2BH_4$$

One of the important properties characteristic of the metal borohydrides is their high volatilities, enabling them to be pumped out of the reaction mixture and purified by trap-to-trap sublimation. The vapor pressures increase with higher atomic number of the metal. $Th(BH_4)_4$, which sublimes at 120 °C under vacuum, exerts a pressure of 0.2 mmHg at 150 °C,[2b] while neptunium and plutonium borohydrides easily sublime at −10 °C. $Np(BH_4)_4$ has a vapor pressure of 10 mmHg at 25 °C making it the most volatile compound of tetravalent Np known to date. $Pu(BH_4)_4$ appears to exhibit a vapor pressure similar to that of $Np(BH_4)_4$.

The synthesis of $Pa(BH_4)_4$ follows that of $Th(BH_4)_4$ by Hoekstra and Katz,[2b] but the reaction tube was modified by the addition of a demountable cold finger from which the $Pa(BH_4)_4$ could be removed in an inert atmosphere drybox. $Pa(BH_4)_4$ is an orange, air-sensitive solid sublimable at 55 °C under vacuum. X-ray powder diffraction photographs have shown that it is isomorphous with the uranium and thorium borohydrides. Its tetragonal unit cell with $a = 7.54$ (3) and $c = 13.23$ (5) Å contains four molecules, giving a calculated density of 2.63 g/cm^3.

The method used for making neptunium and plutonium borohydrides differs from that above because their high volatilities require no cold finger and their thermal instabilities demand that the reaction be carried out at a lower temperature and for a shorter time. We have found that carrying out the reaction at 0 °C for 4 h works well, after which time the $An(BH_4)_4$ and unreacted $Al(BH_4)_3$ are collected in −78 and −196 °C traps, respectively. Yields were increased by returning the unused $Al(BH_4)_3$ to the reaction tube for another 4-h period and repeating this procedure several times until no more $An(BH_4)_4$ was obtained. An earlier attempt to make $Np(BH_4)_4$ was reported[7] in which only a green, nonvolatile solid was obtained in the reaction vessel. The solid was probably a mixture of NpF_4, mixed neptunium fluoroborohydrides, or lower neptunium borohydrides due to improper reaction conditions. Hoekstra and Katz[7] noted a color change in their $PuF_4/Al(BH_4)_3$ reaction vessel from tan to blue-green, the same color change that we observe in ours; however, their $Pu(BH_4)_4$, if it did form, must have decomposed before collection, as they obtained no volatile Pu compound.

$Np(BH_4)_4$ is a dark green, pyrophoric liquid which melts at 14.2 °C. It must be kept in a greaseless storage tube under liquid nitrogen since it decomposes in the liquid phase fairly rapidly at 25 °C transforming into a yellow, nonvolatile solid with the evolution of H_2 and B_2H_6. This observation suggests that $Np(BH_4)_3$ is formed. At higher temperatures a shiny, metallic mirror is obtained which may be Np metal or NpB_4. $Pu(BH_4)_4$ is a bluish black liquid with properties very similar to $Np(BH_4)_4$ but decomposes more rapidly in the liquid phase.

Diffraction patterns recorded with a low-temperature x-ray powder camera show that $Pu(BH_4)_4$ and $Np(BH_4)_4$ are isomorphous and have a new tetragonal crystal structure type, with $a = 8.59$ (1) and $c = 6.1$ (2) Å at −20 °C for the Pu compound and $a = 8.54$ (5) and $c = 6.1$ (2) Å at −150 °C for the Np compound. The low accuracy of the c dimensions is the result of strong preferred orientation of the crystals and absence from the films of reflections with l values >2. The unit cell contains two metal atoms at 0,0,0 and ½,½,½. No reflections were observed which indicate any deviation from body-centered symmetry. The diffraction data do not define the boron and hydrogen positions.

Each metal atom has two metal atom neighbors at 6.1 Å and eight more at 6.8 Å. These distances indicate that the solid is monomeric, like $Zr(BH_4)_4$[8] and $Hf(BH_4)_4$,[3b] rather than polymeric with borohydride bridges like those in $U(BH_4)_4$.[3a] The molecular volumes (225, 222, 186, 201, and 211 Å^3, respectively, for the Pu, Np, U, Zr, and Hf compounds) suggest

Table I. Physical Properties of the Actinide Borohydrides and Hafnium Borohydride

Compd	Color	Stability (20 °C)	Mp, (°C)	Vapor pressure (mmHg)/°C)	M^{4+} radius, Å	Solid	Gas phase molecular symmetry	Density, g/cm^{-3}
$Th(BH_4)_4$[a]	White	Stable	203 dec	0.05/130	0.972[d]	Polymeric	T_d?	2.56
$Pa(BH_4)_4$	Reddish Orange	Stable	Dec		0.935[d]	Polymeric	T_d?	2.63
$U(BH_4)_4$[b,c]	Dark Green	Very slow dec	Dec	0.3/34	0.918[d]	Polymeric	T_d	2.71
$Np(BH_4)_4$	Bluish Green	Dec	14	10/25	0.903[d]	Monomeric	T_d	2.21
$Pu(BH_4)_4$	Bluish Black	Dec	~14	~10/25	0.887[d]	Monomeric	T_d	2.20
$Hf(BH_4)_4$[a,e]	White	Very slow dec	29	15/25	0.79	Monomeric	T_d	1.86

[a] Reference 2a. [b] Reference 2b. [c] Reference 3a. [d] G. T. Seaborg, "Encyclopedia of Chemical Technology", Vol. 1, 3rd ed, Wiley, New York, N.Y., 1978. [e] Reference 9a.

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