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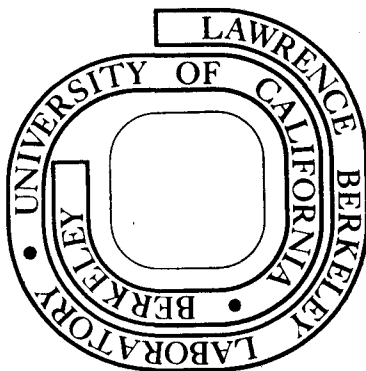
John G. Reynolds and Norman M. Edelstein

December 1976

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THE SYNTHESES, OPTICAL AND MAGNETIC PROPERTIES OF TETRAKIS (DI N-PROPYLAMIDO)URANIUM(IV), TETRAKIS(DI N-BUTYLAMIDO) URANIUM(IV), TETRAKIS(DI N-PROPYLAMIDO)THORIUM(IV), AND TETRAKIS(DI N-BUTYLAMIDO)THORIUM(IV), VOLATILE LIQUID AMIDES[†]

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ABSTRACT

The thorium and uranium alkyl amides, $M[N(CH_2CH_2CH_3)_2]_4$ and $M[N(CH_2CH_2CH_2CH_3)_2]_4$, M = Th and U, have been prepared and isolated. These extremely air-sensitive compounds are liquids at room temperature and distillable under high vacuum at temperatures less than 100°C. The proton magnetic resonance spectra, the optical spectra, and the temperature-dependent magnetic susceptibilities (T = 4.2°K - 100°K) of the two uranium compounds are reported. The spectroscopic and magnetic properties of the uranium compounds are very similar to those of $U(N(C_2H_5)_2)_4$.

INTRODUCTION

Transition metal amides have been utilized as reactive intermediates in the synthesis of transition metal alkoxides, thiols, and organometallic derivatives.[1] Recently, we have reported many new uranium amides, which are not only useful as extremely reactive intermediates,[2,3] but exhibit novel physical properties.[4-7] In the solid state, these new uranium compounds have exhibited monomeric,[6] dimeric,[4] trimeric,[5] and tetrametric[7] molecular units, with the U atoms being bridged by N atoms. The coordination about the U atom is four, five, or six in the crystals, while in solution the coordination about the U atom depends on the complexing ability of the solvent. In order to extend this work, we now report the preparation and isolation of the actinide amides, $U[N(CH_2CH_2CH_3)_2]_4$, $U[N(CH_2CH_2CH_2CH_3)_2]_4$, and their thorium analogs. These compounds are liquids at room temperature, and their physical and solution properties are markedly similar to those of $U(NEt_2)_4$[4,8] and $Th(NEt_2)_4$,[9] respectively.

EXPERIMENTAL

Solvents

All solvents were dried and deoxygenated by refluxing with sodium and benzophenone under purified argon.

Reagents and Synthesis

All reactions and manipulations were done either under vacuum or in a purified argon atomosphere. The amides were purchased from the Aldrich Chemical Company. N-butyl lithium was purchased from Alpha-Ventron Corporation and used as delivered.

LiNR$_2$. These compounds were prepared by the slow addition of the amine mixed with pentane (dried with KOH, then drierite) to n-butyl lithium in hexane at ice-bath temperatures. The resulting precipitate was filtered and vacuum dried.

UCl$_4$ and ThCl$_4$. These compounds were purchased from ROC/RIC and used as delivered.

U(N(CH$_2$CH$_2$CH$_3$)$_2$)$_4$. 10 grms of UCl$_4$ (0.0264 mol) and 11.2 grms (0.105 mol) of LiN(CH$_2$CH$_2$CH$_3$)$_2$ were placed in a 250 ml schlenk flask. Approximately 100 ml of diethyl ether was transferred into the flask under vacuum at liquid N$_2$ temperature. The heterogeneous mixture was warmed to room temperature and continously stirred during the reaction. The reaction times varied from 24 hours to 7 days. The formation of a characteristic green solution and a LiCl ppt indicated the completion of the reaction. The solution was then filtered and the filtrate reduced to a high viscosity liquid by vacuum evaporation. This residue was placed in a distillation apparatus and distilled between 40°C and 50°C at 10^{-4} mm Hg, yielding a green liquid product. The yields for this compound and the others reported in this paper were about 30-40%. Anal.[10] (in % by weight). Calculated for U(N(CH$_2$CH$_2$CH$_3$)$_2$)$_4$: U, 37.3; C, 45.1; N, 8.77; H, 8.77. Found: U, 37.58; C, 44.69; N, 8.63; H, 8.54.

U(N(CH$_2$CH$_2$CH$_2$CH$_3$)$_2$)$_4$. This compound was synthesized on the same scale as above but with the following minor changes. Reaction time was extended to 8 weeks. The characteristic green solution was not observed for at least four weeks. The sublimation temperature range was 90 - 100°C. Temperatures above 110°C caused noticeable decomposition, distilling over some volatile decomposition products. Anal. (in %

by weight) calculated for $U(N(CH_2CH_2CH_2CH_3)_2)_4$: U, 31.73; C, 51.20;
N, 7.47; H, 9.60. Found: U, 31.85; C, 50.95; N, 7.23; H, 9.51.

$Th(N(CH_2CH_2CH_3)_2)_4$. This compound was synthesized by the same
method as above but with the following changes. Reaction time was
at least 7 days. The reaction was complete when a slight yellow tinge
to the diethyl ether solution appeared since the $ThCl_4$ and LiCl
suspensions are virtually undistinguishable under these condi-
tions. The sublimation temperature range was 60 - 70°C 10^{-4} mm Hg,
yielding a clear light yellow liquid. This compound appeared to be
photo-sensitive for the product slowly darkened after distillation.
Anal. (in % by weight) calculated for $Th(N(CH_2CH_2CH_3)_2)_4$: Th, 36.70;
C, 45.57; N, 8.86; H, 8.86. Found: Th, 37.03; C, 45.16; N, 8.86;
H, 8.86.

$Th(N(CH_2CH_2CH_2CH_3)_2)_4$. This compound was synthesized by the
same method as above except with the following changes. Reaction time
was 6 weeks. Sublimation temperature was 90 - 100°C at 10^{-4} mm Hg, and
temperatures above 110°C caused noticeable decomposition. The dis-
tillation produced a clear light yellow liquid, also sensitive to
heat and light. Anal. (in % by weight) calculated for
$Th(N(CH_2CH_2CH_2CH_3)_2)_4$: Th, 31.18; C, 51.60; N, 7.53; H, 9.68.
Found: Th, 30.86; C, 51.32; N, 7.38; H, 9.51.

Physical Measurements

Proton magnetic measurements were obtained on a Varian T-60
spectrometer, a Varian NV-14 spectrometer, or a Varian 220 MHz
spectrometer with Nicolet Fourier transform modifications. The
latter two spectrometers were equipped with variable temperature

probes. The NV-14 spectrometer was equipped with a Minimite model 238 temperature control unit equipped with a minimite thermocouple having an accuracy of $\sim$1.0°C. The Varian 220 MHz spectrometer was calibrated by a methanol standard. Samples were prepared by dissolving the purified amides in d_8 THF or d_8 toluene to give solutions $\sim$1M. The neat samples were prepared from the freshly distilled liquids and placed in Wilmad PS-503 NMR tubes. The NV-14 spectrometer required an internal lock of $\sim$10% by volume of benzene or TMS. All NMR tubes were sealed under vacuum.

The optical measurements were obtained on a Cary 17 spectrometer at room temperature. The liquids were placed into shortened melting point capillaries by a syringe. These previously tared capillaries were weighed on a Cahn electrobalance. The capillaries were then broken in a volumentric flask and sufficiently diluted to give the appropriate concentrations of $\sim$.02 M. The solutions were then syringed into .5 cm cells and then sealed with silicon stopcock grease. The spectra were taken immediately with a 0.5 cm cell containing the solvent as a reference.

Magnetic susceptibility measurements were obtained with a PAR Model 155 vibrating sample magnetometer used with a homogeneous magnetic field produced by a Varian Associate 12 inch electromagnet capable of a maximum field strength of 12.5 Kg. The magnetometer was calibrated with $HgCo(CNS)_4$.[11] A variable temperature liquid helium dewar produced sample temperatures in the range 1.5 - 100°K which were measured by a calibrated GaAs diode placed approximately one-half inch above the sample. The liquids were placed in calibrated Kel-F screw top susceptibility capsules which were weighed on a Cahn electrobalance. The filled

capsules were stored in schlenk tubes under argon, and were transferred to the susceptibility apparatus under flowing N_2. Samples of ~0.1 grm were used.

DISCUSSION

The reaction used for the syntheses of these new actinide amides is the same as employed previously for the large majority of transition metal amides:[12]

$$MCl_4 + 4LiNR_2 \xrightarrow{\text{Et}_2\text{O}} M(NR_2)_4 + LiCl \downarrow$$
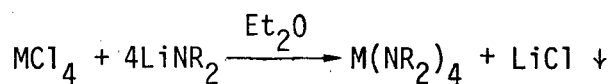
$$M = U, Th$$

$$R = -CH_2CH_2CH_3, -CH_2CH_2CH_2CH_3 \quad .$$

Table 1 lists some of the physical properties of these actinide amides. Although the di-n-propyl and di-n-butyl actinide amides are the first reported actinide amides which are liquid at room temperature, this behavior is common in d-transition-metal amides.[1,12] The distillation temperatures of the corresponding thorium and uranium dialkyl amides are quite similar.

The pmr spectra of the uranium and thorium amides in d_8 toluene and d_8 THF are given in Table 2. The proton spectra of the thorium amides are almost identical to those of the free ligands as expected for a diamagnetic Th^{4+} ion. The pmr spectra of the U amides can be classified into two groups depending on the solvent used. The proton spectra of the U amides in d_8 toluene have peaks asymmetrically placed about TMS, and significantly shifted from the corresponding diamagnetic positions. As the distance of the proton from the U atom is increased,

the magnitude of the shift decreases. Also, resolution of the spin-spin coupling occurs at the γ carbon protons, suggesting that at this distance the effects of line width broadening due to the very fast electronic relaxation time of the paramagnetic U^{4+} ion, are much diminished. If we assume that the U species in toluene solution is monomeric as found for the $U(NEt_2)_4$ compound,[8] then the most likely structure for the U n-alkyl amides is tetrahedral. For this symmetry the pseudo contact term vanishes, and only the Fermi contact hyperfine interaction contributes to the paramagnetic shift.[13] This interaction would be of a similar magnitude for each of the U n-alkyl amide compounds and would account for the similarily of the paramagnetic shifts in the series.

The same argument may be used for the pmr of the U n-alkyl amides in ether solvents. Table 2 shows the great similarity of the shifts for the three compounds. It appears that the ether solvents complex the U amides and the solution structures are very similar. Therefore, the g value anisotropy, the pseudo-contact shifts, and the Fermi contact term are similar for each of the compounds, which results in similar pmr spectra for each of α, β, etc., protons in the alkyl chain for each compound.

The pmr spectra of the neat compounds are also given in Table 2 These relative splittings and the resolution of the multiplets are the same as found in toluene solution but there is an absolute shift of 10-13 ppm upfield in the line positions due to the effects of the bulk susceptibility of the solution. These observations support our assumptions that the U n-alkyl amides (and $U(N\phi_2)_4$) do not coordinate with hydrocarbon solvents and that they are monomeric at room temperature in

these solvents.

We have reported previously a possible monomer-dimer equilibrium for $U[NEt_2]_4$ in d_8 toluene solution, which would change the symmetry about the U ion.[4] (The solid state dimer has approximately C_{3v} symmetry about the U^{4+} ion). Figure 1 shows the pmr spectra of $U[N(CH_2CH_2CH_3)_2]_4$ in d_8 toluene at various temperatures. The monomeric species is clearly displayed at high temperatures but the changes in the spectra at low temperatures show definite signs of broadening and exchange. Unlike the $U(NEt_2)_4$ system where the dimer is observed clearly at $\sim$-43°C, the U n-propyl amide shows only broadening to $\sim$-60°C at which point it freezes out of solution. The U n-butyl amide exhibits similar behavior. These observations may be explained by a less favorable geometry due to greater steric hinderance for the formation of the dimeric species of the U n-propyl and n-butyl amides than for $U(NEt_2)_4$. Further work is underway on the temperature dependence of the pmr spectra.

The optical and near ir spectra of the uranium n-propyl amide in various solvents at room temperature are shown in Fig. 2 and tabulated for both uranium amides in Table 3. These spectra are almost identical to those of the previously published $U(NEt_2)_4$ and $U(N\phi_2)_4$ in the same solvents.[4,6] As in the pmr spectra we suggest the spectra in the ether solvent are due to a U molecule associated with the complexing ether solvent molecules, whereas in hydrocarbon solvents the spectra are due to the uncomplexed tetrahedral U molecule. The almost identical spectrum for each of the uranium n-alkyl amides in the same solvent shows that changing the alkyl chain   little effect on the f-f transitions. The major differences in the spectra come from changes in the first coordination sphere as shown by the effects of the ether solvent.

The inverse of the magnetic susceptibility of $U[N(CH_2CH_2CH_2CH_3)_3]_4$ in the temperature range $4.2°K - 100°K$ is shown in Fig. 3. A similar curve is found for $U[N(CH_2CH_2CH_3)_2]$. The data for the three n-alkyl amides is collected in Table 4. In all cases there is Curie behavior down to $\sim30°K$ ($20°K$ for $U(NEt_2)_4$) after which the inverse of the susceptibility tends to become less temperature dependent. The symmetry in the solid state of the two new uranium amides is unknown but the susceptibility data could be due to a ground state singlet with a doublet state approximately ~35 cm^{-1} higher in energy. The effective moments of all the amides in the temperature range where they follow the Curie law are similar.

CONCLUSION

We have succeeded in the synthesis and characterization of some new U and Th alkyl amides, one of which was reported as being non-distillable in the original report of $U(NEt_2)_4$.[8] The uranium n-alkyl amides and $U(N\phi_2)_4$ have very similar spectral properties in various solvents. The ether solvents appear to complex each of the uranium n-alkyl amides in the same fashion, while the hydrocarbon solvents do not appear to complex. The low temperature magnetic susceptibilities in the solid state are similar. The analogous Th n-alkyl amides have been synthesized and appear to be light-sensitive. These amides exhibit the expected diamagnetic behavior. Even though a number of new uranium and thorium amides have been synthesized and can be purified by distillation, there are d-transition metal amides which sublime or distill for which the analogous actinide amides have not been isolated.[12,15] This may be because the U amides tend to oligomerize and/or be more thermally unstable than the corresponding d-transition metal amides. Much work remains to be done on these interesting systems.

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Table 1.   Physical Properties of Some Uranium Amides

Compound	Phase[a]	Distillation Temp.[b]
$U(N(CH_2CH_3)_2)_4$[4,8]	solid	40° - 50° C
$U(N(CH_2CH_2CH_3)_2)_4$	liquid	40° - 50° C
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	liquid	90° - 100° C
$Th(N(CH_2CH_3)_2)_4$[9]	solid	40° - 50° C
$Th(N(CH_2CH_2CH_3)_2)_4$	liquid	50° - 60° C
$Th(N(CH_2CH_2CH_2CH_3)_2)_4$	liquid	90° - 100° C
$U(N(C_6H_5)_2)_4$[6]	solid	dec.[c]
$U_3(CH_3NCH_2CH_2NCH_3)_6$[5]	solid	dec.

a - at room temperature

b - at less than 10^{-4} mm Hg pressure

c - decomposition without sublimation

Table 2. Proton Magnetic Resonance Spectra of Some Uranium Amides[a] with respect to TMS (ppm).

Compound	Solvent	α	β	γ	δ	Temperature
$U(N(CH_2CH_3)_2)_4$ [4]	d_6 Benzene	-13.0[b]	+5.4[c]	—	—	24°C
$U(N(CH_2CH_2CH_3)_2)_4$	d_8 toluene	-8.4(s)	+1.9(s)	-.4(t)	—	25°C
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	d_8 toluene	-9.4(s)	+3.1(s)	-.3(m)	+.5(t)	19°C
$U(N(CH_2CH_3)_2)_4$ [4]	d_8 THF	+18.2	+13.8	—	—	24°C
$U(N(CH_2CH_2CH_3)_2)_4$	d_8 THF	+19.8(s)	+12.9(s)	+8.04(t)	—	26°C
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	d_8 THF	+17.9(s)	+11.6(s)	+6.5(s)	+2.6(t)	19°C
$U(N(CH_2CH_2CH_3)_2)_4$	neat	+1.1(s)	+11.4(s)	+9.3(t)	—	25°C
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	neat	+3.5(s)	+16.5(s)	+13.3(m)	+14.1(t)	25°C
$Th(N(CH_2CH_2CH_3)_2)_4$	d_6 Benzene	-2.7(t)	-1.1(m)	-.5(m)	—	25°C
$Th(N(CH_2CH_2CH_2CH_3)_2)_4$	d_6 Benzene	-2.95(t)	-1.3(m)	-1.0(m)	-.7(t)	25°C

a. α = α carbon proton, β = β carbon proton, γ = γ carbon proton, δ = δ carbon proton, t = triplet, s = singlet, m = multiplet.

b. - = downfield relative to TMS.

c. + = upfield relative to TMS.

Table 3. Peak Positions and Extinction Coefficients of $U(N(CH_2CH_2CH_3)_2)_4$ and $U(N(CH_2CH_2CH_2CH_3)_2)_4$ in Various Solvents.

Compounds	Solvent	Peak 1 $\lambda,\mu m$	ε	2 $\lambda,\mu m$	ε	3 $\lambda,\mu m$	ε	4 $\lambda,\mu m$	ε	5 $\lambda,\mu m$	ε	6 $\lambda,\mu m$	ε
$U(N(CH_2CH_3)_2)_4$ [a]	Hexane	.704	50	b	—	c	—	1.104	25	1.188	25	c	—
$U(N(CH_2CH_2CH_3)_2)_4$	Pentane	.705	39	b	—	c	—	1.105	24	1.180	24	c	—
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Pentane	.702	45	b	—	c	—	1.100	25	1.170	24	c	—
$U(N(CH_2CH_3)_2)_4$ [a]	Benzene	.692	47	b	—	c	—	1.090	27	1.172	26	c	—
$U(N(CH_2CH_2CH_3)_2)_4$	Benzene	.705	44	b	—	c	—	1.105	32	1.180	30	c	—
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Benzene	.705	45	b	—	c	—	1.095	30	1.170	28	c	—
$U(N(CH_2CH_3)_2)_4$ [a]	Et_2O	.638	28	.660	24	.718	15	.990	20	1.070	32	1.302	19
$U(N(CH_2CH_2CH_3)_2)_4$	Et_2O	.638	22	.658	19	.710	17	1.000	16	1.078	28	1.310	12
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	Et_2O	.640	24	.665	19	.710	17	1.005	17	1.070	30	1.305	18

a. From Reference 4.
b. Peaks were not split into two components.
c. Peaks masked by solvent bands.

Table 4.   Temperature Dependent Susceptibility Values for Some
Uranium Amides.

Compound	C_M	μ_{eff}(BM)	Θ(°K)	Temp.(°K)
$U(N(CH_2CH_3)_2)_4$[4]	1.052	2.74	-4.8	20-100
$U(N(CH_2CH_2CH_3)_2)_4$	1.00	2.69	7.2	30-102
$U(N(CH_2CH_2CH_2CH_3)_2)_4$	.74	2.44	2.2	27-84
$U(N(C_6H_5)_2)_4$[6]	1.00	2.84	24.8	40-90

FIGURE CAPTIONS

Fig. 1. Proton magnetic resonance spectra of $U[N(CH_2CH_2CH_3)_2]_4$ in d_8 toluene at various temperatures.

Fig. 2. Optical spectra of $U[N(CH_2CH_2CH_3)_2]_4$ in various solvents at room temperature.

Fig. 3. Inverse susceptibility of $U[N(CH_2CH_2CH_3)_2]_4$ versus temperature. The straight line is the calculated inverse susceptibility in that temperature range with the parameters obtained from a least-square fit as given in Table 4.
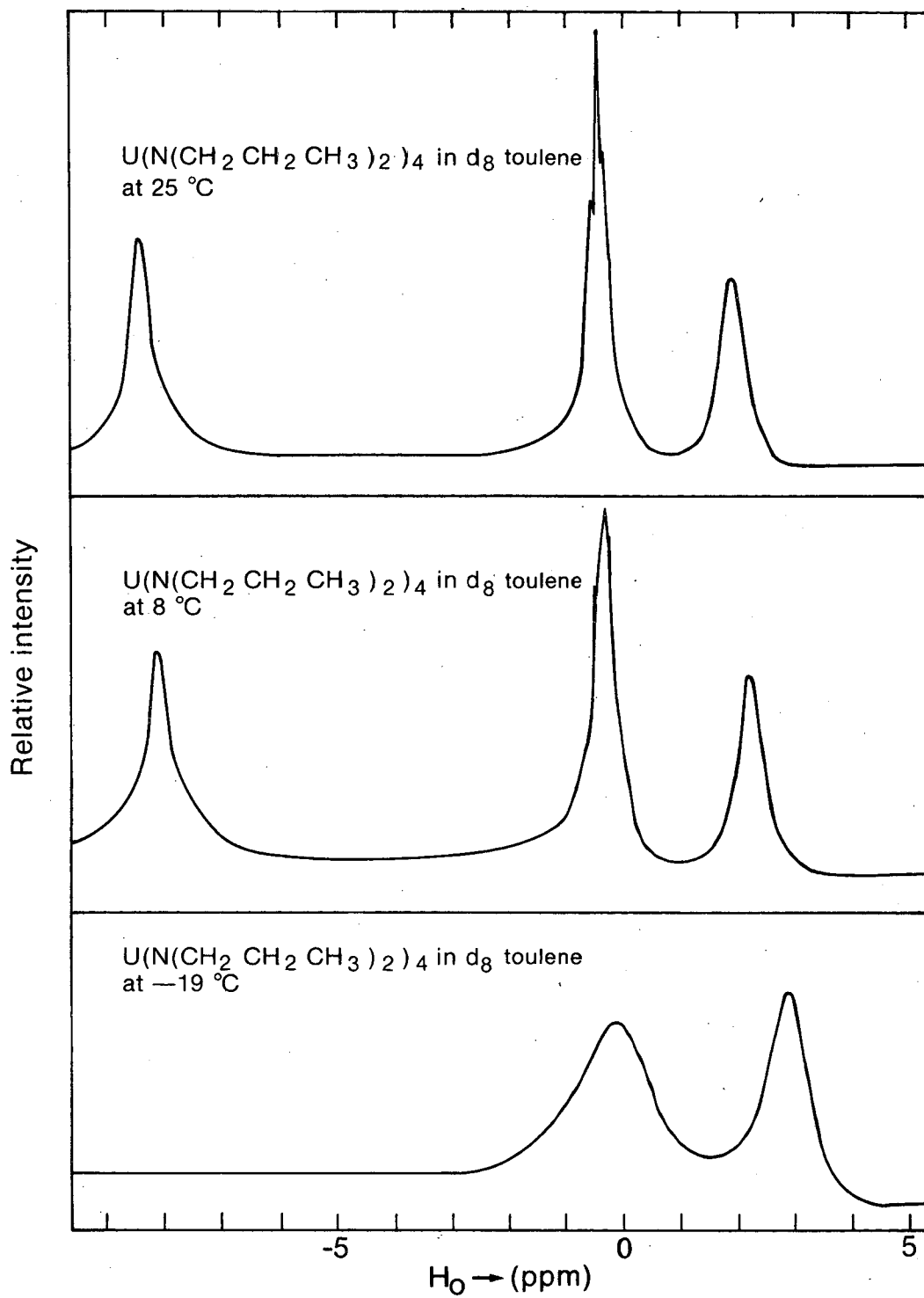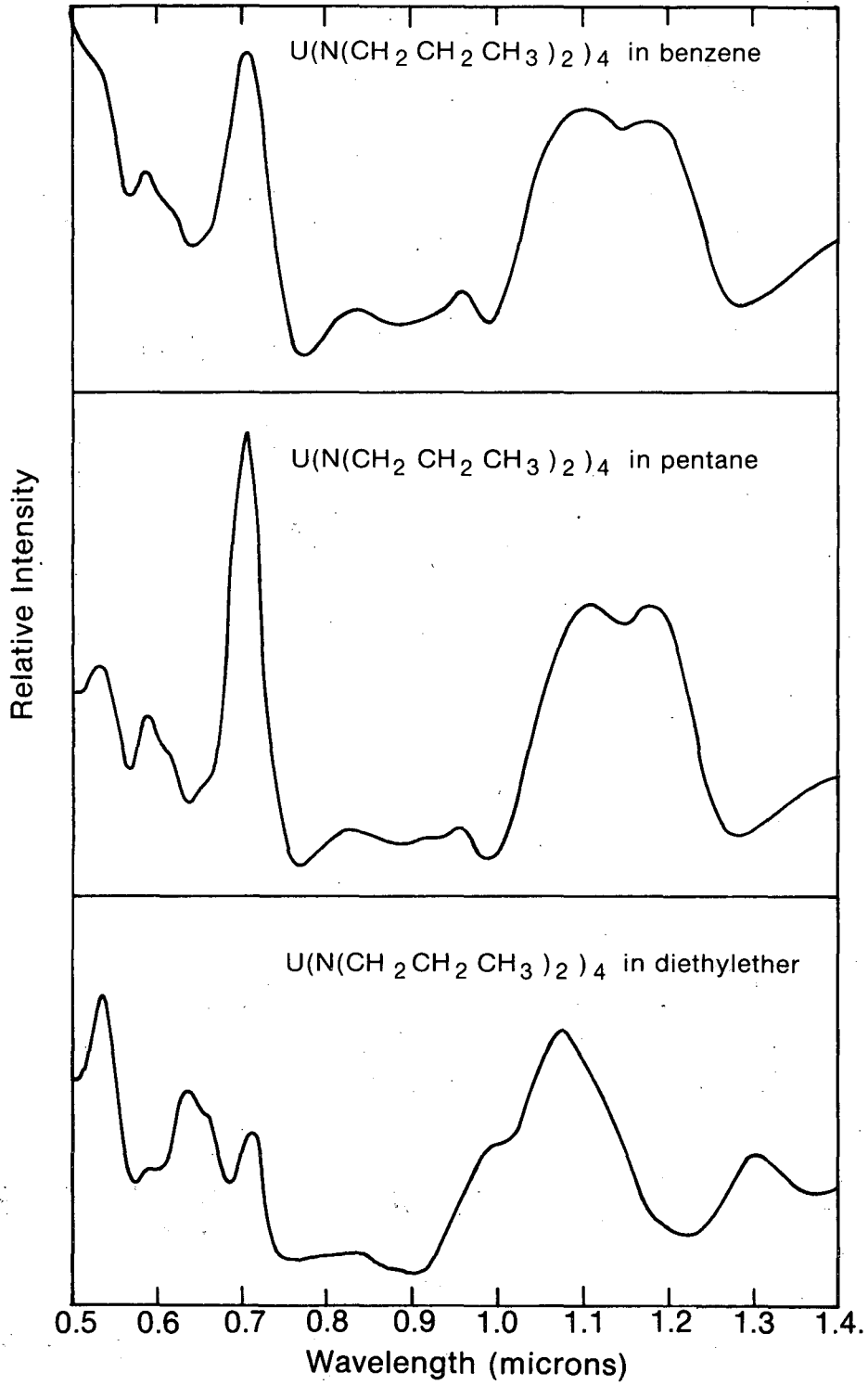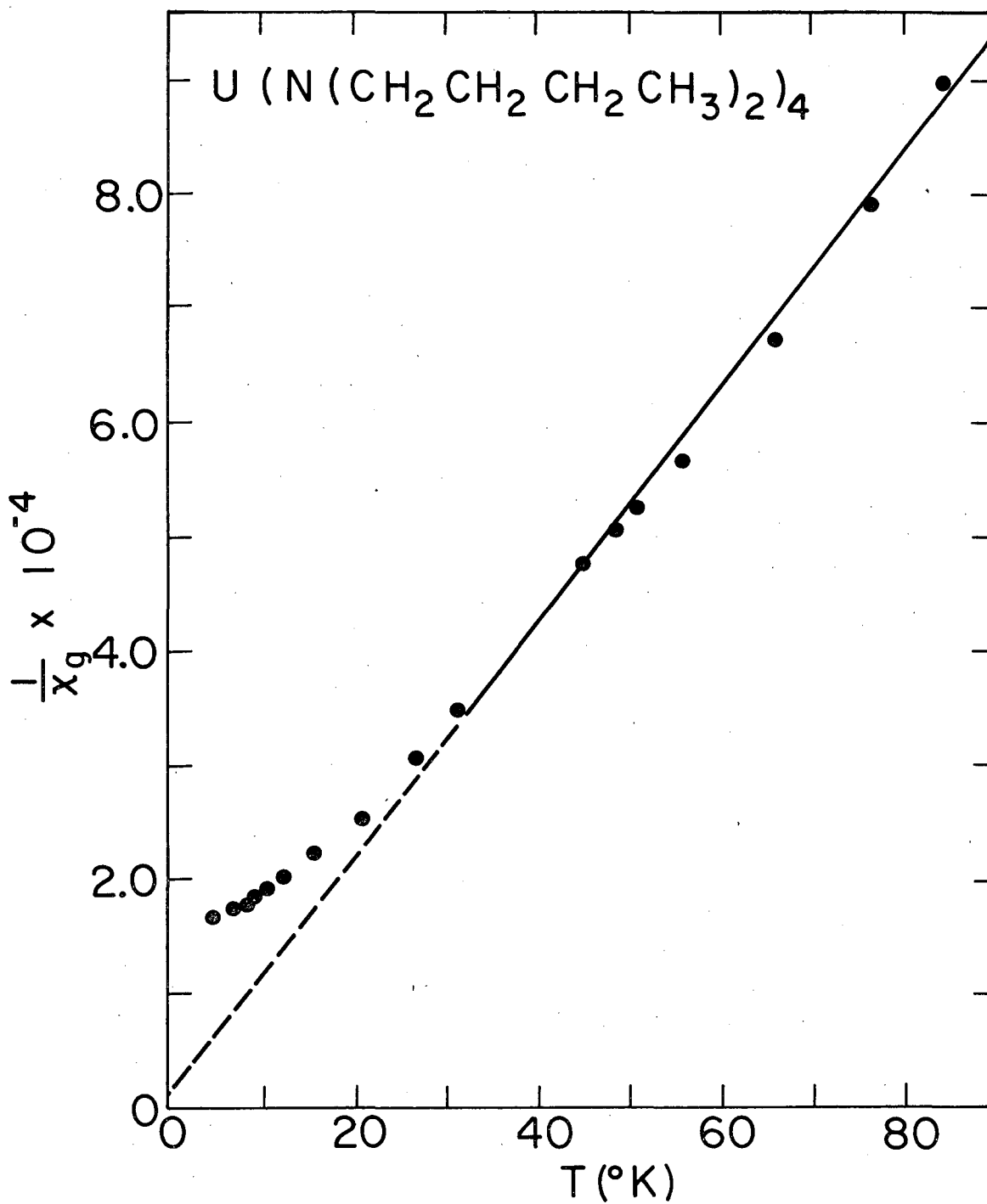
Fig. 1

XBL 7611-4389

Fig. 2

XBL7611-4390

$$U(N(CH_2 CH_2 CH_2 CH_3)_2)_4$$

Fig. 3

XBL 7611-4393