Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

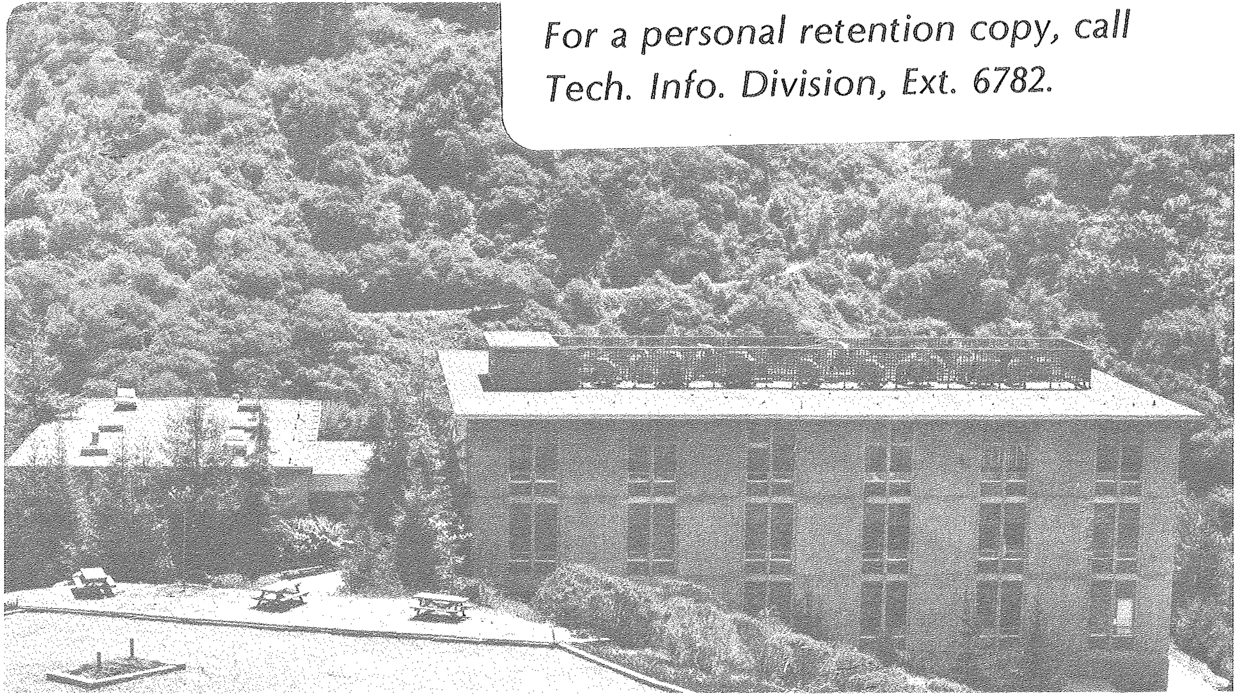
Materials & Molecular
Research Division

Submitted to Inorganic Chemistry

BIS-π-(CYCLOBUTENOCYCLOOCTATETRAENE)URANIUM(IV)

Wayne D. Luke, Stuart R. Berryhill, and
Andrew Streitwieser, Jr.

November 1980



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

Bis-π-(Cyclobutenocyclooctatetraene)uranium(IV)

Wayne D. Luke,[1] Stuart R. Berryhill[2]
and Andrew Streitwieser, Jr.*

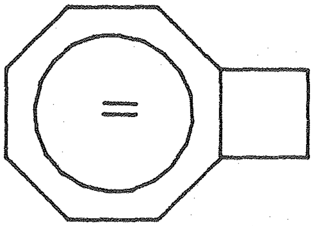
Department of Chemistry, University of California
and
Materials and Molecular Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720

Abstract

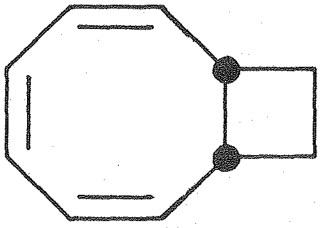
The title compound 3 was prepared by reaction of cyclobutenocyclooctatetraene dianion 1 with UCl_4, and characterized by visible, IR, NMR and mass spectra. The magnetic susceptibility shows Curie-Weiss dependence to 15°K and is temperature independent between 15°K and 4.2°K. Variable temperature ^1H NMR from -80°C to +70°C, as well as chemical trapping experiments show no evidence for opening of the cyclobutene ring to a quinodimethane moiety. The ^1H NMR spectrum is analyzed in terms of pseudocontact and contact contributions. It is shown that $\mu_\perp^2 \neq 0$ and that $\mu_\parallel^2 - \mu_\perp^2 = 12.5\ \mathrm{B.M.}^2$

Introduction

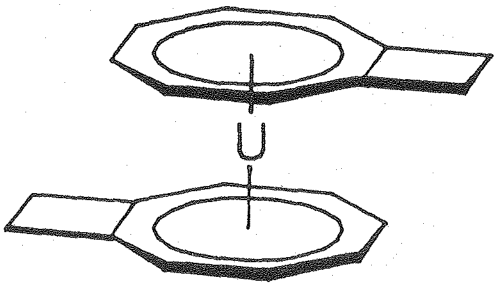
The substituent effects of a wide variety of alkyl and hetero atom substituents on the physical properties of uranocene are well documented.[3-5] We now wish to report the synthesis of the first annulated uranocene and the effects of annulation on the uranocene skeleton. Recently Staley and co-workers have investigated the preparation of the annulated cyclooctatetraene dianion **1** by dideprotonation of the corresponding cis-bicyclooctatriene **2**.[6,7] They showed that treatment of **2** with potassium amide in liquid ammonia leads to **1** in high yield. The availability of **1** prompted us to investigate its use in the synthesis of an annulated uranocene. In this paper we report the conversion of **1** into the first annulated uranocene, dicyclobutenouranocene, **3**.[8]



1



2



3

XBL 8011-12103

Synthesis and physical properties of dicyclobutenouranocene.

The bicyclooctatriene **2** was prepared as described by Staley and Henry[9] and further purified through its silver nitrate adduct. Attempted deprotonation of **2** with either n-butyllithium/TMEDA or lithium diisopropylamide in THF was unsuccessful; however, treatment of **2** with potassium amide in liquid ammonia according to the Staley procedure[10] afforded **1** as a grey-green solid after evaporation of the solvent. Reaction with UCl_4 in THF gave an air-sensitive dark green crystalline solid which was purified by Soxhlet extraction with pentane.

Mass spectral analysis showed a molecular ion of 498 and principal fragments of 386 (loss of $C_{10}H_{10}$) and 130 ($C_{10}H_{10}$) confirming the dicyclobutenouranocene **3**, structure. Furthermore, controlled air oxidation of **3** produced bicyclo[6.2.0]deca-1,3,5,7-tetraene which was identified by its ^1H NMR spectrum.[11] The visible spectrum of **3** shows the expected bathochromic shift for an alkyl-substituted uranocene with λ_{max} at 623 nm ($\varepsilon = 610$). A comparison of the IR spectrum of **3** with that of uranocene is shown in Table 1.

At 30°C the ^1H NMR spectrum of **3** consists of three singlets with linewidths of about 35 Hz at δ -27.7, -35.9 and -43.8 ppm (upfield from TMS) and two sharp doublets ($J_{H-H} = 9.64$ Hz) at -26.75 ppm and 19.65 ppm. From the linewidths and the splitting pattern, the three singlets can be assigned to the three ring protons and the two doublets to the methylene protons indicating that the methylene groups are fixed with the protons distinguishable as a

Table 1. Infrared spectrum of dicyclobutenouranocene, **3**, in Nujol compared with uranocene.

Uranocene[a,b]	**3**[a]
1730 (w)	
1262 (s)[c]	1262 (m)
	1195 (w)
	1165 (w)
1018 (s)[c]	1120 (s)
	979 (s)
	918 (s)
799 (s)	820 (m)
	818 (s)
	795 (w)
	791 (s)
	780 (m)
720 (s)	718 (vs)

(a) w = weak, m = medium, s = strong, vs = very strong.

(b) For assignments of the ir bands of uranocene, see L. Hocks, J. Goffart, G. Duyckaerts and P. Teyssie, *Spectrochimica Acta*, **30A**, 907 (1974).

(c) broad.

diastereotopic pair with a remarkable shift difference of 46.4 ppm. Although the chemical shifts for the ring protons fall within the region given by various substituted uranocenes, the range from -27.7 to -43.8 ppm is somewhat larger than usual.[12]

The ^{13}C NMR of 3 at 37°C displays three broad resonances at 273, 313 and 326 ppm downfield from TMS and a single sharp resonance at -63.7 ppm upfield from TMS. By analogy with the ring carbon resonance of uranocene (297 ppm) and the methyl resonance of 1,1'-dimethyluranocene (-52.5 ppm), the lowfield resonances in the ^{13}C spectrum of 3 are assigned to the non-quaternary ring carbons and the sharp upfield resonance to the methylene carbon. The quaternary carbon resonance could not be resolved unambiguously.

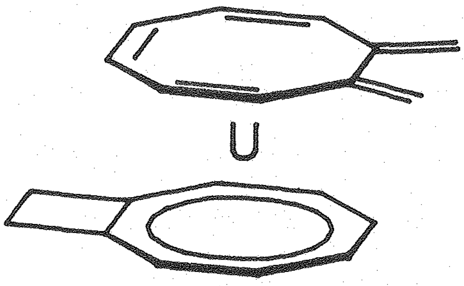
The magnetic susceptibility of 3 was measured via the vibrating magnetometer method over the range of 4.2°K to 100°K to provide the data plotted in Fig. 1. The magnetic susceptibility displays Curie-Weiss behavior from 15°K to 100°K with μ_{eff}=2.36 B. M.; Θ=8.5°K and is essentially temperature independent below 15°K. Susceptibility measurements at 30°C by the Evans method[13] gave a value of $\chi_{AVE}=2.34 \times 10^{-3}$, emu mol^{-1}. This number is in excellent agreement with that extrapolated from the low temperature data, 2.23×10^{-3} emu mol^{-1}. This temperature dependence behavior corresponds well with that of uranocene and several of its derivatives.[14-18]

Discussion

The physical and spectral properties of 3 indicate that annulation exerts little if any perturbation on the uranocene skeleton. Indeed, a recent X-ray crystal structure of 3 has shown that the 8-membered rings in 3 are nearly regular octagons and that the uranium ring carbon distance is identical within experimental error to that in other uranocenes.[19]

Formally, 1 is the 10π-electron homolog of benzocyclobutene. In light of the known temperature dependent benzocyclobutene-o-quinodimethane rearrangement,[20] we searched for a similar cyclobutene-butadiene type equilibrium of the 4-membered rings in 3. Variable temperature ^{1}H NMR from -80°C to 80°C showed no evidence of a ring-opened species. Likewise, attempts to chemically trap a diene-type ring-opened form of the ligand on 3 were unsuccessful. Thus, heating a diglyme solution of 3 with dimethyl acetylenedicarboxylate for 20 hr at 150°C showed no apparent reaction. Attempted trapping with bis-trimethylsilylacetylene and with maleic anhydride also failed. A solution of 3 in bis-trimethylsilylacetylene showed no change in visible spectrum after 7 days at room temperature. However, on heating, the uranocene slowly decomposed; total decomposition occurred after 24 hr at 190°C. Addition of maleic anhydride to a solution of 3 in mesitylene produced decomposition of the uranocene within about 5 min at room temperature. Heating the two solids together resulted in similar decomposition when the maleic anhydride melted. Irradiation of a toluene solution of 3 for 1/2 hr with a 450 watt Hanovia lamp also failed to effect any rearrangement of the ligands in 3.

The foregoing results show that electrocyclic ring opening of the type 3 → 4 is not more facile than for benzocyclobutene itself. Temperatures of the order of 200°C are required for the latter reaction.[20]



4

NMR Analysis of Dicyclobutenouranocene

Nmr studies on uranocenes have recently been reviewed thoroughly.[12] Both contact and pseudocontact shifts have been shown to contribute to the observed isotropic shifts in the ^1H NMR spectra of uranocenes;[21,22] however, some controversy has surrounded the relative magnitudes of each of these components.[23,24] The ring proton isotropic shifts in uranocene and a wide variety of substituted uranocenes are linear in T^{-1} and thus, the pseudocontact component of the ^1H shifts can be evaluated by[25]

$$\delta_{\mathrm{PSEUDOCONTACT}} \quad [\mu_z^2 - 1/2(\mu_x^2 + \mu_y^2)]\frac{\beta^2}{3kT}\,\frac{3\cos^2\theta-1}{R^3} + \frac{(\mu_x^2 - \mu_y^2)}{2}\,\frac{\beta^2}{3kT}\,\frac{\sin^2\theta\cos^2\psi}{R^3} \qquad (1)$$

where R, θ and ψ are the spherical coordinates of the resonating nucleus and μ_i are the principal components of the magnetic moment. In uranocenes having at least a C_3 or greater rotational axis, symmetry dictates that $\mu_y^2 = \mu_x^2$ and eq. 1 reduces to the familiar axial form where $\mu_z^2 = \mu_{\parallel}^2$ and $\mu_{\perp}^2 = \mu_x^2 = \mu_y^2$. Recently, we have shown[12] that $\mu_x^2 \simeq \mu_y^2$ in substituted uranocenes of lower symmetry and thus, the second term of eq. 1 can be effectively neglected in evaluating the pseudocontact shifts in these compounds.

Originally, Edelstein, et. al.,[21] calculated the pseudocontact contribution to the observed isotropic shifts in uranocenes by assuming $\mu_{\perp}^2 = 0$, and $\mu_{\parallel}^2 = 3\mu_{\mathrm{AVE}}^2$. More recently, Fischer, et. al.[23,24] have demonstrated in substituted uranocenes that $\mu_{\perp}^2$ is non-zero but less than $\mu_{\parallel}^2$. The restricted conformational mobility and the fixed spatial orientation of the α protons in **3** suggest that it may be an excellent system for further testing Fischer's proposal.

Contact shifts for α-protons in paramagnetic metallocenes are assumed to arise from hyperconjugative transfer of spin. By locking the alkyl substituents in **3** into a fused 4-membered ring the dihedral angle between the p-orbitals of the 8-membered ring and the methylene C-H bonds is fixed; hence, hyperconjugation and a derived contact shift must be equal for both endo and exo α-protons. Thus, the difference in the observed isotropic shifts for the exo and endo methylene protons must result from differences in the pseudocontact shift, or as eq. 1 shows, differences in the geometry factor for the exo and endo protons, (eq. 2).

$$\frac{(\mu_{\parallel}^2 - \mu_{\perp}^2)}{3} \quad \frac{\beta^2}{3kT} = \frac{\delta_{exo} - \delta_{endo}}{G_{exo} - G_{endo}} \tag{2}$$

In the solid state, the X-ray structure of $\underset{\sim}{3}$ has shown that the two methylene groups are not equivalent whereas solution spectra show them to be equivalent on the NMR tine scale. To evaluate the conformational mobility of the fused ring in $\underset{\sim}{3}$, the ^{1}H NMR spectrum was measured as a function of temperature from -80°C to 80°C, (Fig. 2). Two of the ring protons are linear in T^{-1}, similar to the temperature dependence generally of the ring proton resonances in uranocene and substituted uranocenes,[12] whereas the low-field ring proton resonance and both of the methylene proton resonances are non-linear indicative of temperature dependent conformational mobility.[26] Despite this conformational mobility, their average position in solution can probably be approximated to sufficient accuracy by their average position in the crystal. Taking the average thermally adjusted C-C bond lengths and angles from the crystal structure,[19] a methylene C-H bond length of 1.09A, and a methylene bond angle of 112° (similar to that in benzocyclobutene)[27] (Fig. 3), the calculated geometry factors for the exo and endo protons are, respectively, -0.709×10^{21} cm^{-3} and -16.97×10^{21} cm^{-3}.

Analysis of the isotropic shifts in 3 requires referencing the observed shifts to their position in the spectrum of a corresponding diamagnetic uranocene. The differences between the proton resonances in thorocenes and corresponding cyclooctatetraene dianions are relatively small[28] and both have been used as diamagnetic reference compounds. Referencing the resonances of 3 at 30°C to the corresponding resonances in the dianion 1 affords isotropic shifts of 16.35 ppm (exo), -30.05 ppm (endo), -33.28 ppm, -41.48 ppm, -49.38 ppm (ring). Substitution of these isotropic shifts and the geometry factors for the methylene protons into eq. 2 leads to a value of 12.5 B.M.^{2} for $\mu_{\parallel}^2 - \mu_{\perp}^2$, with corresponding pseudocontact shifts of -2.03 ppm (exo) and -48.5 ppm (endo) and a contact shift of 18.4 ppm. These calculated values show that the difference in the sign of the observed isotropic shifts of the methylene protons results from the fact that the isotropic shift for the exo protons is principally contact in nature whereas the endo isotropic shift is dominated by the pseudocontact component; the "magic angle" lies close to the exo-hydrogen.

The value of $\mu_{\parallel}^2 - \mu_{\perp}^2 = 12.5$ B.M.^{2} is significantly smaller than the value of 17.28 B.M.^{2} derived from the Edelstein, et. al.,[21] assumption of $\mu_{eff}^2 = \mu_{\parallel}^2$, $\mu_{\perp}^2 = 0$. There is some uncertainty in our estimate because of our assumption that the 4-membered ring is, on the average, coplanar with the 8-membered ring in 3. Actually, the 4-membered ring is tilted slightly towards the uranium.[29] Nevertheless, the chemical shift differences of the exo and endo α-protons is so large that this effect should introduce but little error into our analysis. There seems little doubt that $\mu_{\perp} \neq 0$

in uranocenes in agreement with the results of Fischer et al.[23,24] Our value of $\mu_{\parallel}^2 - \mu_{\perp}^2$ is somewhat larger than the value of 8.78 B.M.^{2} derived by Fischer et al. but the assumed geometries required in their derivation add uncertainty to the lower value such that their approach is not inconsistent with ours. As a result of $\chi_{\perp} \neq 0$, early work on factoring the isotropic shift of the ring protons in uranocene underestimated the magnitude of the contact shift. We also note in this connection that a recent theoretical study of uranocene by Warren[30] for a $J_z = \pm 4$ ground state gave a non-zero $\chi_{\perp}$ result but less than $\chi_{\parallel}$. Using our value of $\mu_{\parallel}^2 - \mu_{\perp}^2 = 12.5$ B.M.^{2}, the pseudocontact and contact shifts for uranocene ring protons are -8.3 and -34.2 ppm, respectively (for $G_i = -2.34 \times 10^{21}$ cm^{-3}). Thus, this study confirms that both contact and pseudocontact interactions contribute to the observed isotropic shifts in uranocenes.

Acknowledgment. This work was supported in part by NSF grant nos. CHE76-82170 and CHE78-24084 and in part by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-ENG-48.

Experimental

All solvents were carefully dried over sodium/benzophenone (THF) or LAH or CaH_2 (hydrocarbons), vacuum transferred, and stored in an argon atmosphere in a Vacuum Atmospheres continuously recirculating glove box. All reactions were run under an atmosphere of dry nitrogen or argon. Visible spectra were obtained on a Cary 118 spectrophotometer and IR with a Perkin Elmer 297 infrared spectrophotometer. All melting points are uncorrected. The ^1H NMR were obtained on the Berkeley FT system operating at 180 MHz and equipped with a variable temperature probe whose temperature can be regulated to ±0.3°C. The ^{13}C spectra were obtained on a Brucker WH-90FT spectrometer. Magnetic susceptibility measurements were made with a Princeton Applied Research vibrating-sample magnetometer operating in the field of a Varian Associates magnet capable of field strengths to 12.5 kilo-gauss, at Lawrence Berkeley Laboratories under the direction of Dr. N. M. Edelstein. A liquid helium dewar and a PAR Cryogenic Control gave access to temperatures in the 4.2-100 K range. Analyses were performed by Chemalytics, Inc., Tempe, Arizona or the Analytical Services Laboratory, University of California, Berkeley.

cis-Bicyclo[6.2.0]deca-2,4,6-triene (**2**). -- To 300 mL of liquid ammonia in a 3-neck flask was added 1.39 g (0.2 mole) of lithium wire (1% sodium) in short strips. To the resulting deep blue solution was added 10.4 g (0.1 mole) of freshly distilled cyclooctatetraene. The yellowish suspension was stirred for 1.5 hr at -40°. To this suspension was added dropwise 18.8 g (0.1 mole) of 1,2-dibromoethane in 20 mL of ether. The reaction mixture was

was stirred for 4 hr at ca. -33°, and the ammonia was allowed to evaporate leaving a dark brown residue which was taken up as a suspension in 200 mL of saturated aqueous NH_4Cl. The aqueous mixture was extracted with 3 x 100 mL of ether, and the combined ether extracts were washed with water and dried over $MgSO_4$. The ether solution was filtered and concentrated, and the residue was distilled. The product was collected at 62-65° (5 mm); yield 6.1 g (46%); NMR (CCl_4): δ 5.77 (s, 6H, vinyl), 2.87-3.27 (m, 2H, bridgehead) and 1.70-2.40 (m, 4H, cyclobutyl).

Silver nitrate adduct of 2. -- A solution of 0.5 g of 2 in 15 mL of ether was poured into 50 mL of 25% aqueous $AgNO_3$. A fluffy white solid formed at the interface. The mixture was shaken well and suction filtered. The solid was air-dried and recrystallized from absolute ethanol; mp 169-170° dec. An analytical sample was recrystallized a second time.

Anal. Calcd. for $C_{10}H_{12}NO_3Ag$: C, 39.76; H, 4.00; N, 4.64. Found: C, 39.86; H, 4.06; N, 4.61.

Bicyclo[6.2.0]deca-1,3,5,7-tetraene dipotassium 1. -- cis-Bicyclo[6.2.0]deca-2,4,6-triene, 2 (3.0 g, 23 mmols) was added to a solution of potassium amide (from 1.78 g, 46 mmols, of potassium) in 160 mL of liquid ammonia at 035°. The resulting red-orange solution was stirred for 1 hr at -35°, and allowed to warm slowly to room temperature. During warming, the evaporating ammonia was swept out of the reaction vessel with a stream of nitrogen. The solid residue was further dried at high vacuum for several hrs; NMR (THF-d_8): δ 3.30 (s, 4H, cyclobutyl) and 5.58 (s, 6H, COT ring). ^{13}C NMR: δ 34.7 (CH_2), 87.7, 90.3, 91.5, 103.2 (C-R), ppm.

Dicyclobutenouranocene, 3. -- Solid potassium salt 1 (from above) was dissolved in 40 mL of THF, and the solution was transferred to a uranocene reactor. This solution was cooled to -78°, and a solution of 4.32 g (11.5 mmols) of uranium tetrachloride in 25 mL of THF was added. The reaction mixture was allowed to warm to room temperature, the solvent was vacuum transferred, and the solid residue was dried overnight under high vacuum. Extraction with pentane gave 4.7 g (83%) of dark green crystalline material.

Anal. Calcd. for $C_{20}H_{20}U$: C, 48.20; H, 4.05. Found: C, 47.90; H, 3.88.

Reaction of 3 *with dimethyl acetylenedicarboxylate*. -- Into a tube fitted with a stopcock were placed 0.25 g (0.5 mmol) of 3, 10 mL of diglyme and 0.15 g (mmol) of freshly distilled dimethyl acetylenedicarboxylate. The system was sealed and placed in an oil bath at 150°C for 20 hrs. After the reaction period the contents of the tube were centrifuged to remove polymer resulting from polymerization of the acetylene. A visible spectrum of the supernatant liquid was identical with that of the starting material.

Reaction of 3 *with maleic anhydride*. -- Addition of 0.5 g of triply sublimed maleic anhydride to 0.1 g of 3 in 25 mL of mesitylene afforded a brown solution in 5 min. Removal of the solvent by vacuum transfer left a brown solid. A mass spectrum of this material indicated a small amount of starting material was present.

A 100 mL flask was charged with 0.2 g of 3 and 5 g of triply sublimed maleic anhydride. Slow heating of this material produced decomposition of the green uranocene as soon as the maleic anhydride melted. Removal of the anhydride by high vacuum followed by mass spectral analysis of the remaining brown residue showed no uranocene to be present.

Reaction of 3 with bis-trimethylsilylacetylene. -- A 100 mL Fischer-Porter bottle was charged with 0.1 gm of 3 and 15 ml of freshly distilled bis-trimethylsilylacetylene. The reaction mixture was stirred for 5 days under Ar at 30°C followed by 12 hr at 150 ± 3°C and 12 hr at 190 ± 3°C. Monitoring the reaction by visible spectra showed no decomposition after 5 days at 30°C, 30% decomposition after 12 hr at 150°C and total decomposition after 12 hr at 190°C.

Photolysis of 3. -- A solution of 3 in toluene-d_8 in a pyrex NMR tube was strapped to the quartz well of a photolysis apparatus and irradiated for 2 hr with a 400 Watt medium pressure Harnovia lamp. An ^{1}H NMR spectrum just before and just after irradiation showed no change.

References

1. Current address: Eli Lilly, West Lafayette, Indiana.
2. Current address: Chemistry Department, California State University, Long Beach.
3. Streitwieser, A. Jr.; Harmon, C. A. *Inorg. Chem.* **1973**, *12*, 1102.
4. Harmon, C. A.; Bauer, D. P.; Berryhill, S. R.; Hagiwara, K.; Streitwieser, A. Jr. *Inorg. Chem.* **1977**, *16*, 2143.
5. streitwieser, A. Jr.; Burghard, H.P.G.; Morrell, D. G.; Luke, W. D. *Inorg. Chem.* **1980**, *19*, 1863.
6. (a) Staley, S. W.; Cramer, G. M.; Orvedal, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 7433; (b) Staley, S. W.; Linkowski, G. E.; Heyn, A. S. *Tetrahedron* **1975**, *31*, 1131; (c) Staley, S. W.; Cramer, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 5051.
7. Compare: (a) Osborn, C. L.; Shields, T. C.; Shoulders, B. A.; Krause, J. T.; Cortez, H. V.; Gardner, P. D. *J. Am. Chem. Soc.* **1965**, *87*, 3158; (b) La Lancette, E. A.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 1941; (c) Staley, S. W.; Linkowski, G. E. *J. Am. Chem. Soc.* **1976**, *98*, 5010; (d) Staley, S. W.; Linkowski, G. E.; Fox, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4818.
8. By analogy with ferrocene nomenclature we have named this compound as an annulated derivative of the parent uranocene skeleton.
9. Staley, S. W.; Henry, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 7612; see also Cotton, F. A.; Degasello, A. *J. Am. Chem. Soc.* **1972**, *94*, 2142.

10. Staley, S. W.; Cramer, G. M.; Orvedal, A. W. *J. Am. Chem. Soc*. **1974**, *96*, 7433.

11. Elix, J. A.; Sargent, M. V.; Sondheimer, F. *J. Am. Chem. Soc*. **1967**, *89*, 180.

12. Luke, W. D.; Streitwieser, A. Jr. in "Lanthanide and Actinide Chemistry and Spectroscopy", N. M. Edelstein, ed., ACS Symposium Series 131, Washington, D.C., 1980, p. 93.

13. Evans, D. F. *J. Chem. Soc*. **1959**, 2003.

14. Karraker, D. G.; Store, J. A.; Jones, E. R. Jr.; Edelstein, N. M. *J. Am. Chem. Soc*. **1970**, *92*, 4841.

15. Karraker, D. G. *Inorg. Chem*. **1973**, *12*, 1105.

16. Amberger, H. D.; Fischer, R. D.; Kanellakopolus, B. *Theoret. Chim. Acta*. **1975**, *37*, 105.

17. Edelstein, N. M.; LaMar, G. N.; Mares, F.; Streitwieser, A. Jr. *Chem. Phys. Lett*. **1971**, *8*, 399.

18. Edelstein, N. M.; Streitwieser, A. Jr.; Morrell, D. G.; Walker, R. *Inorg. Chem*. **1976**, *15*, 1397.

19. Zalkin, A.; Templeton, D. H.; Berryhill, S. R.; Luke, W. D. *Inorg. Chem*. **1979**, *18*, 2287.

20. For examples see (a) Oppolzer, W. *J. Am. Chem. Soc.* **1971**, *93*, 3833; (b) DeCamp, M. R.; Levin, R. H.; Jones, M. *Tet. Lett*. **1974**, 3575; (c) Hillard, R. L. III; Vollhardt, K.P.C. *J. Am. Chem. Soc*. **1977**, *99*, 4058; (d) Funk, R. L.; Vollhardt, K.P.C. *J. Am. Chem. Soc*. **1976**, *98*, 6755.

21. Edelstein, N. M.; LaMar, G. N.; Streitwieser, A. Jr. *Chem. Phys. Lett*. **1971**, *8*, 399.

22. Streitwieser, A. Jr.; Dempf, D.; LaMar, G. N.; Karraker, D. G.; Edelstein, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 7343.

23. Fischer, R. D. in "Organometallics of the f-Elements", Marks, T. J.; Fischer, R. D. eds., D. Reidel, Boston, Mass. 1979, p. 337.

24. Fischer, R. D.; Spiegl, A. W.; Dickert, F. *Chem. Ber.*, in press.

25. Kurland, R. J.; McGarvey, B. R. *J. Magnetic Resonance*, **1970**, *2*, 286.

26. Luke, W. D.; Berryhill, S. R.; Streitwieser, A. Jr. to be published.

27. Gunther, H.; Jikeli, G.; Schmicker, H; Prestien, J. *Angew Chem. Int. Ed. Engl.* **1973**, *12*, 762.

28. LeVanda, C.; Streitwieser, A. Jr. *Inorg. Chem.*, in press.

29. Compare the similar situation in 1,1',3,3',5,5',7,7'-octamethyluranocene: Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1973**, *12*, 458.

30. Warren, K. D. *Structure and Bonding*, **1977**, *33*, 97.

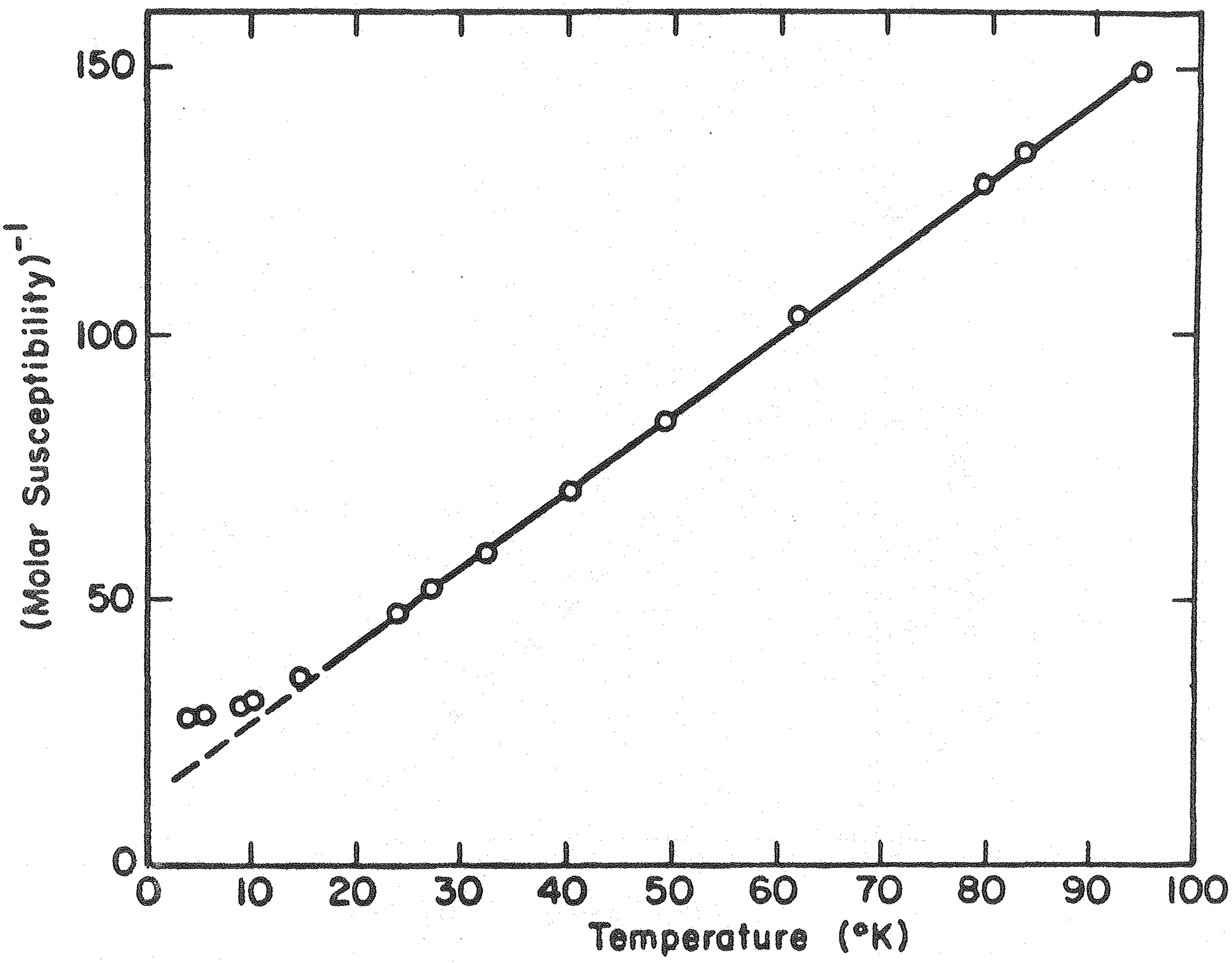


Fig. 1. The reciprocal of the molar magnetic susceptibility as a function of temperature (Curie-Weiss plot). The least squares line based as indicated on the points shown yields the Curie constant = 0.690 emu °K mol^{-1}, θ = 8.5°K, μ_{eff} = 2.36 B.M.

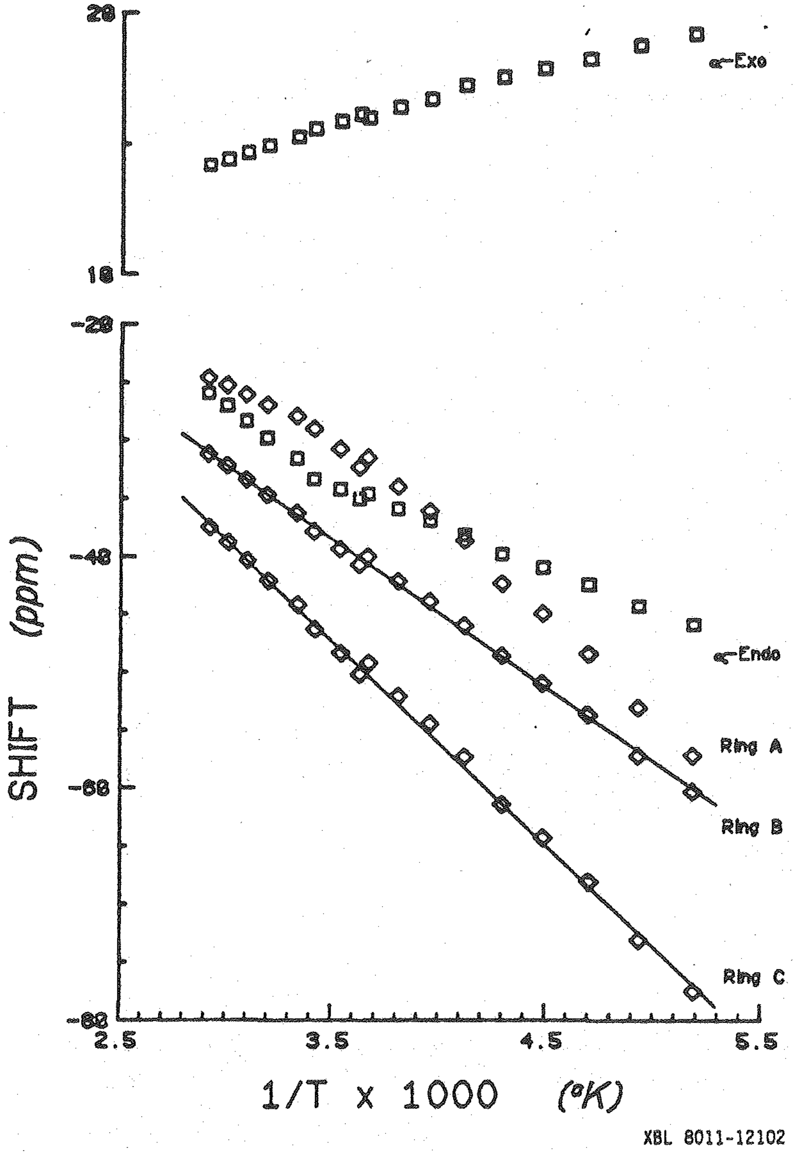
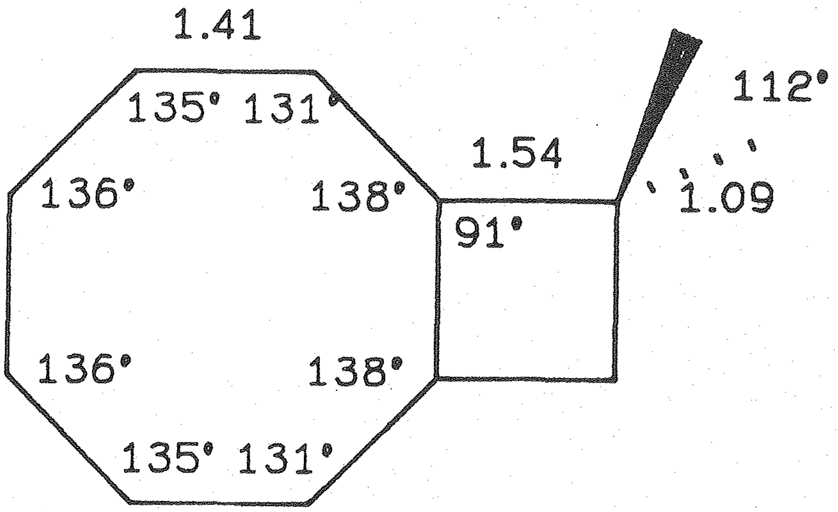


Fig. 2. Isotropic shifts of 3 relative to the dianion as a function of reciprocal temperature. The protons on the 8-membered ring are not assigned and the resonances are labeled A,B,C in order of increasing field. Linear relations for the chemical shifts of B and C are given by: $\delta(B) = 6.25 \pm 0.48 - (12809 \pm 123)/T$; $\delta(C) = 14.05 \pm 0.77 - (17582 \pm 197)/T$.



XBL 801-7885

Fig. 3. Average structure for the ligand of 3 used for calculation of the geometry factors.