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Some Recent Advances in Uranocene Chemistry

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Among the recent advances in uranocene chemistry have been the synthesis and spectral study of several unique compounds that help to characterize the bonding and ring–ring interactions in f-block sandwich compounds. One of these new compounds is the uranocene structure derived from benzocyclooctatetraene. The nature of the bonding in uranocenes has been a matter of interest and controversy for some years [1]; structural data fit an ionic model [2, 3] but photoelectron spectra [4], nmr studies [5], Xα calculations [6] and Mössbauer spectroscopy [7] suggest substantial covalency. A large number of substituted uranocenes have been prepared for such studies but most substituents (*e.g.*, alkyl groups) constitute a relatively small perturbation of the electronic system of the [8]annulene system. For this reason the benzo[8]annulene system is of especial interest; in benzocyclooctatetraene radical anion, for example, a substantial fraction of the spin density is delocalized into the benzene ring [8].

Benzocyclooctatetraene, *1*, was prepared by a modification of the method of Elix and Sargent [9]; 7,10-dihydrobenzocyclooctatetraene, *2*, derived from trapping with butadiene the cyclooctatrienyne intermediate produced by reaction of bromocyclooctatetraene with sodium amide, was dehydrogenated with dichlorodicyanobenzoquinone (DDQ). Benzo[8]annulene dianion [10, 11], *3*, was produced by reduction of *1* with potassium or potassium naphthalide in THF. The reaction of *3* with uranium tetrachloride in THF gave a 20% yield of the desired dibenzouranocene together with extensive reduction [12].

Dibenzouranocene, *4*, exhibits some other unusual properties. Unlike the usual 4-band cascade at about 620 nm typical of uranocenes, *4* has only a broad absorption at 624 nm with a single shoulder at 650 nm. The compound is much less soluble than most substituted uranocenes and is more like uranocene itself. Moreover, the compound has a low temperature coefficient of solubility that makes recrystallization difficult. Nevertheless, crystals suitable for X-ray analysis were obtained by slow crystallization. The resulting structure [13] shows the two benzene rings to be almost eclipsed with each other. This pattern results in a disordered crystal in which the [8]annulene and benzene ring sites are interchanged. The structure could nevertheless be worked out and is shown in Figs. 1 and 2. An extremely important feature of this structure is the centrosymmetric location of the uranium between the [8]annulene rings despite the almost eclipsed structure of the benzo-substituents. In an ion triplet model with U^{+4} between two rings of *3*, the uranium would be expected to lie about 0.3–0.4 Å away from this centrosymmetric position towards the benzenes. Thus, the observed results provide the first structural evidence for significant ring–metal covalency in *4*.

Related compounds were also prepared. Bis(benzo[8]annulene)thorium(IV), *5*, was prepared in a manner analogous to the uranium compound. Reduction of the Diels–Alder adduct *2* also gave a

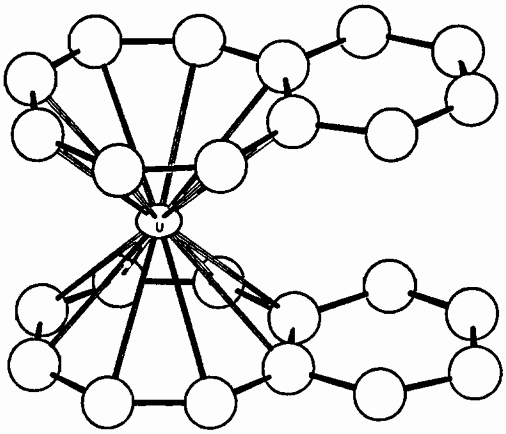

Fig. 1. X-ray structure of dibenzouranocene, *4* (ref. 13).

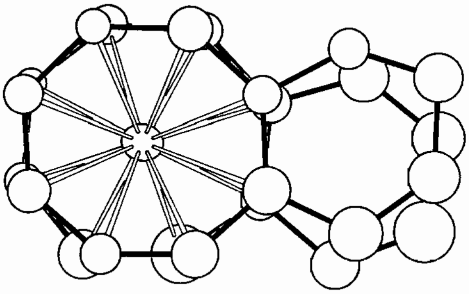

Fig. 2. Top view of dibenzouranocene (ref. 13).

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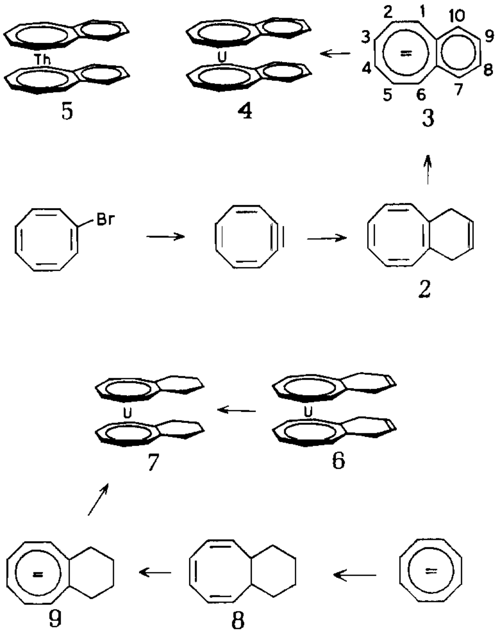
dianion which formed a uranocene derivative, *6*, with UCl_4in a normal fashion. Attempted dehydrogenation to *4* by oxidation yielded only uranium salts and recovered neutral ligand. Hydrogenation of *6*, however, did proceed normally to yield bis(tetrahydrobenzo[8]annulene) uranium *7*. Use of deuterium gave the corresponding deuterium compound which by nmr analysis showed the deuterium to be incorporated 70% exo and 30% endo. This constitutes the first stereoselective reaction on a uranocene. The low selectivity shows that the other ring provides only a minor steric barrier to reaction, perhaps because of conformational twisting of the alicyclic ring. Authentic *7* was prepared by the route used previously to prepare dicyclopentenouranocene [14]. Reaction of the dilithium adduct of COT with 1,4-dibromobutane in liquid ammonia gave cis-bicyclo[6.4.0]dodeca-2,4,6-triene, *8*, which was deprotonated with KNH_2/NH_3 to the dianion and treated with UCl_4 to yield *7*. The reactions are summarized in Scheme 1.

Analysis of the ^{1}H-nmr spectrum of the thorium compound *5*, as summarized in Tables I and II, yields the essential features of that previously reported [10, 11] for the dipotassium salt of the dianion *3* with two notable differences. The chemical shift of the protons (H8 and H9) of the benzene removal of electron density from this periphery of the ring system. Other chemical shift changes are relatively small but the vicinal coupling constants in the [8]annulene ring, J(1,2), J(2,3), J(3,4) (Table II) are all significantly higher for the thorium compound. These changes also suggest an increase in the electron population of the 8-membered ring. These results are consistent with the thorium compound *5* being isostructural with the uranium system *4*. Even in a covalent model the rings and the central metal are highly charged; thus, the high positive charge of the centrally located thorium pulls electrons from the periphery of the benzene portion into the [8]-annulene ring. We note also that the vicinal couplings in the benzene ring are still consistent with aromatic

TABLE II. Coupling Constants in ^{1}H-NMR Spectra.

J_{ij} (Hz)	*3*	*5*
1,2	11.86	13.6
1,3	0.11	0.1
1,4	−0.35	−0.4
1,5	0.10	0.1
1,6		0.0
2,3	11.21	13.2
2,4	0.66	0.7
2,5	−0.20	−0.2
3,4	10.22	11.0
7,8	8.51	8.2
7,9	1.55	1.3
7,10	0.47	0.5
8,9	5.80	5.5



5 4 3 2 7 6 9 8

Scheme 1.

TABLE I. ^{1}H-NMR Spectra.

Cpd: Pos	*3*[a]	*5*	*4*[b,c]	*6*[d,e,f]	*7*[e,g]	*11*[d,h]
(1)	6.610	6.738	−48.87	−30.37	−30.83	−48.00
(2)	6.258	6.283	−19.38	−33.17	−32.71	−16.81
(3)	5.892	5.984	−24.80	−39.11	−38.82	−23.27
(7)	7.692	7.756	−10.57	−20.99[i] 14.73[j]	−22.52[i] −3.31[j]	−11.56
(8)	6.067	7.016	−12.69	−8.49	−16.68[i] +6.18[j]	−13.67

[a] Ref. 19. [b] 30 °C. [c] Assignment of 1, 2, 3 based on spin decoupling; assignment of 7 and 8 based on analysis of contact and pseudocontact components (see text). [d] At 27 °C. [e] The [8]annulene resonances are not assigned to specific positions. [f] J(7,7) = 17.09 Hz. [g] At 29 °C. [h] COT ring, −37.51. Other assignments are by analogy to *4*. [i] Endo. [j] Exo.

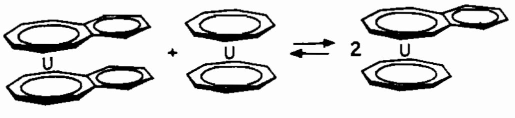
character for the [8]annulene ring according to Gunther's criterion [15].

The uranium compound *4* is paramagnetic and the ^{1}H-nmr spectrum shows the large contact and pseudo contact shifts typical of uranocenes [5]. Nmr absorption peaks of uranocenes are usually so broad that couplings are obscured but in the case of *4* some such couplings were observed and permitted assignments of chemical shifts by decoupling experiments. For the 8-membered ring irradiation at each resonance gave distinct narrowing of bands for the adjacent hydrogens. The changes in the benzo ring, however, were at the threshold of detection, and the hydrogens were assigned by the following argument.

The pseudocontact shift for uranocene has been estimated to be about -8 ppm based on the calculated geometric factor ($G_i = [3 \cos^2\theta - 1]/R^3$) = -2.34×10^{21} cm^{-3} and $\mu_\parallel^2 - \mu_\perp^2 = 12.5$ BM^2 [5]. The geometry about the [8]annulene ring in *4* is essentially the same as in uranocene and the same value of the pseudo-contact shift should apply to all three positions, 1-, 2-, and 3- of *4*. Consequently, the large differences in chemical shifts among these positions reflect the variations in contact shift resulting from the spin density distribution. If the electronic structure of *4* can be regarded as one in which electron density is donated from ligand dianion *3* to a central U^{+4}, the resulting spin polarization should give a spin density distribution in the ligand resembling that of the radical anion of benzocyclooctatetraene. The same picture emerges from an electronic structure derived from interaction of the u and g combinations of the HOMOs of two molecules of *3* and suitable f- and d- orbitals of U^{+4}. Accordingly, we expect a correlation between the contact shifts and the hyperfine coupling constant (hfcs) of the radical anion. The comparisons in Table III show an excellent parallelism between the two sets of numbers. The G_i value for the 8-proton (benzo β-position) has substantially lower magnitude than for the 7-proton (benzo α-position) reflecting its greater distance from uranium, yet the assigned hfsc is much greater for 8- than for 7-. Best agreement is found for assigning the nmr values as given in Tables I and III; this assignment produces a small contact shift for the 7-proton and a substantially larger one for the 8-proton. From the esr comparison the spin density and the contact shift should be the same for positions 8- and 2-. The smaller value found for 8- could indicate the same kind of electron depletion from the periphery deduced from the thorium compound *5* (*vide supra*).

The proton nmr spectra of *4* show the linear 1/T dependence of chemical shifts typical of uranocenes [5] (Fig. 3).

One significant use made of the nmr spectra was the determination of the equilibrium constant for ligand exchange between *4* and uranocene *10*. We reported previously that uranocenes undergo rapid ligand exchange with cyclooctatetraene dianions [16]. This observation implies that two uranocenes will equilibrate their ligands in the presence of some dianion and led to the following experiment: a crystal of K_2COT was added to an nmr sample of *4* in 50:50 THF-d_8: toluene-d_8. The resulting mixture showed the nmr bands of *4* and uranocene plus a series of bands ascribed to the mixed ring system *11*. The spectrum remained unchanged over several hours. Absolute concentrations could only be estimated (10^{-3} *M*) but only relative concentrations are required to evaluate the unitless equilibrium constant, $K = [11]^2/[4][10]$ for the equilibrium:



4 10 11

The experimental value, K = 7.1, is significantly larger than the simple statistical value of K = 4. This result means that any attraction between the benzene rings in *4* is more than offset by steric effects. Consequently, the almost eclipsed structure of crystalline *4* is clearly a resultant of crystal packing forces. This equilibration experiment is made possible by the large chemical shift range of uranocenes such that the nmr spectra of mixed ring uranocenes are generally distinctly different from those of the homo-ring analogs. The determination of additional such equilibrium

TABLE III. Analysis of nmr Spectrum of **4** (30 °C).

Pos.	δ	Isotropic shift[a]	G_i 10^{21} cm^{-3}	Contact shift[c]	Pseudo-contact shift	α[d]
1	−47.88	−54.6	−2.34	−8.3	−46	0.183
2	−18.94	−25.2	−2.34	−8.3	−17	0.082
3	−24.28	−30.3	−2.34	−8.3	−22	0.125
7	−10.57	−18.3	−5.05	−17.9	0	0.019
8	−12.69	−19.7	−3.68	−13.1	−7	0.082

[a] Based on nmr of **5** as the diamagnetic reference. [b] Geometric factor = $(3 \cos^2\theta - 1)/R^3$ using structure of *4* (ref. 21). [c] Calculated from G_i (ref. 6). [d] Hfsc from esf spectrum of radical anion of **1** (ref. 9).

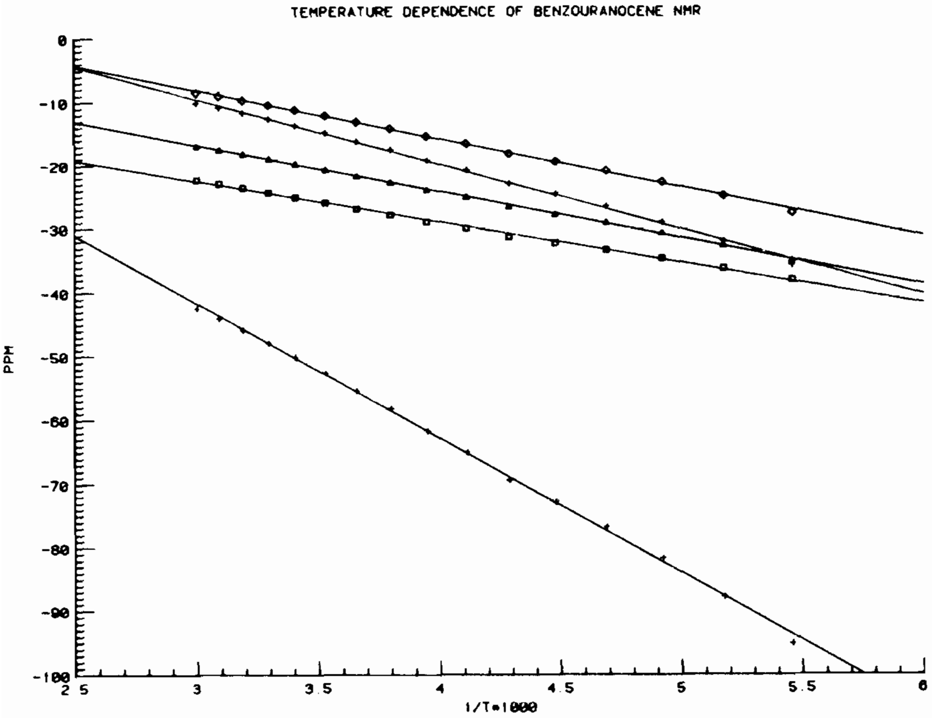


Fig. 3. Nmr δ of *4* vs. 1/T.

constants will undoubtedly provide valuable quantitative data concerning ring–ring interactions in metallocenes.

The relationship between contact shift and esr hyperfine coupling constants found for the benzouranocene system does not apply straightforwardly to alkyluranocenes, perhaps because the alkyl groups do not introduce a sufficient perturbation of the [8]annulene system. There are large variations in contact shift for different hydrogens and these have been identified for primary alkyl substituents. Some examples are summarized in Fig. 4. All of the primary alkyl substituted uranocenes examined (methyl, ethyl, n-propyl, n-butyl, neopentyl) show the same ring hydrogen pattern as indicated in Fig. 4. The 5-hydrogen is readily identified by its relative intensity. The remaining positions were assigned by deuterium labeling experiments [5].

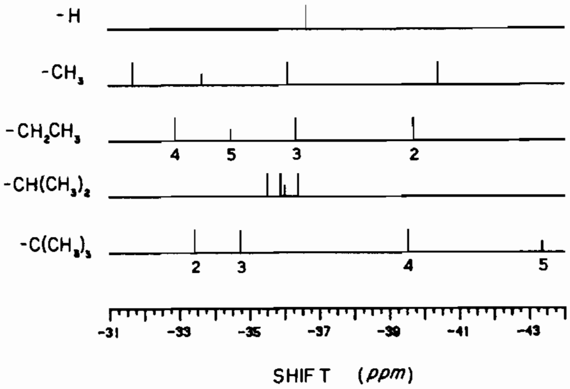
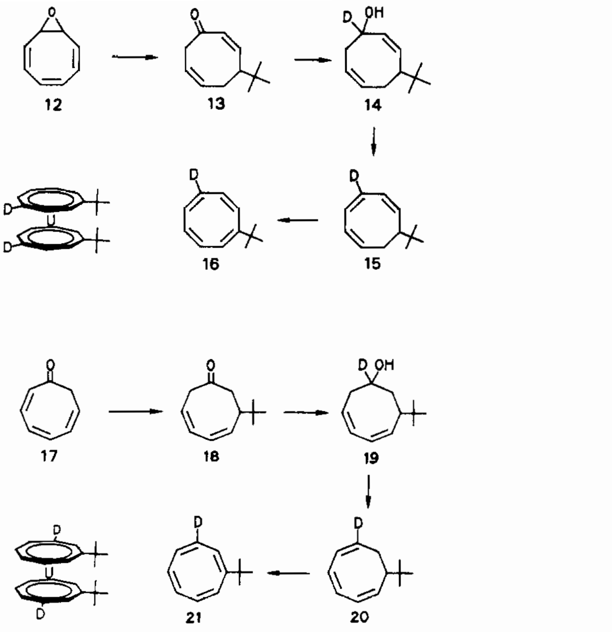


Fig. 4. 1,1′-Dialkyluranocene ring protons at 30 °C.

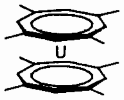
As shown in Fig. 4, the pattern for t-butyl is much different. The highest field proton is now H-5 rather than the proton closest to the substituent, H-2. To assign the remaining positions, specifically deuterated t-butylcyclooctatetraenes were prepared as outlined in Scheme 2. Cyclooctatetraene oxide, *12*, on reaction with t-butyllithium gives the cyclooctadienone *13* which with lithium aluminum deuteride gives a mixture of the *cis* and *trans* alcohols *14*. Dehydration with thionyl chloride yields the t-butylcyclooctatriene *15* which can be deprotonated by careful reaction with sodium amide in THF. Oxidation of the resulting dianion with iodine yields the deuterated t-butylcyclooctatetraene-4-d, *16*, which was converted to the corresponding uranocene. t-Butylcyclooctatetraene-3-d, *21*, was prepared in a similar fashion from cyclooctatrienone, *17*. Reaction with t-butylcuprate gave the conjugate addition product *18* which underwent the analogous sequence of reduction to the alcohols *19*, dehydration to *20* and deprotonation and oxidation to *21*, which was converted to the uranocene. The nmr results gave the assignments shown in Fig. 4 [17]. These assignments agree with those made earlier [5] on a very tentative basis.

The contrasting patterns of primary alkyl and tert-butyl compared with the rather small effect of



Scheme 2.

isopropyl suggest a steric source. The single crystal X-ray structures of octamethyluranocene, *22* [18], dicyclobuteneuranocene, *23* [19], and dicyclopentenouranocene, *24* [20], show the substituents bent in slightly toward the central metal. Models indicate that a similar bending for a t-butyl group would cause one of the substituent hydrogens to come within Van der Waals distance of a ring-hydrogen on the opposite ring. Accordingly, we suggest that the t-butyl group instead is bent away from the central metal. For isopropyl the two effects are equal and opposite and we suggest that such secondary alkyl substituents are bound in the 8-membered ring plane and are not bent appreciably up or down.



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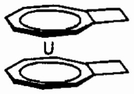

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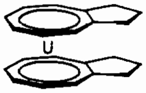

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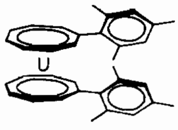
Thus, the pattern of ring hydrogen chemical shifts appears to be dependent on whether the ring substituent is bent towards or away from the central uranium. Because the [8]annulene ring geometry remains essentially constant in all of these structures, the effect clearly is a contact shift effect that depends on spin density. Moreover, the average shift is little different from that of uranocene itself; that is, the total amount of spin density in the [8]annulene ring is essentially constant—it is simply redistributed depending on the bending of the ring alkyl substituent. The reason for this effect—that is, the mechanism coupling the alkyl bending to spin density distribution—is still unknown.

A dramatic demonstration of the validity of the phenomenological effect is found in some results with 1,1′dimesityluranocene, *25* [21].



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Mesitylcyclooctatetraene has been reported [22] but only in poor yield. We obtained a satisfactory preparation by the reaction of mesitylmagnesium bromide with bromocyclooctatetraene in the presence of bis-(triphenylphosphine)nickel chloride [23]. The product was converted to the uranocene in the usual way. The nmr spectrum was especially distinctive and showed conclusively that the mesityl ring was twisted with respect to the [8]annulene ring. The two *ortho*-methyl groups had widely separated chemical shifts, *endo* at −46 ppm and *exo* at +24. Both remained as sharp resonances over a wide temperature range; thus, the mesityl ring must remain twisted with respect to the [8]annulene ring and the two *ortho*-methyls do not interconvert. This result is not unexpected since the internal angle of the octagonal ring is greater than that of a six-membered ring and the barrier to rotation should be substantially higher than that of the corresponding biphenyl.

o-Tolylcyclooctatetraene was prepared by the Cope [24] procedure of reaction of cyclooctatetraene with *o*-tolyllithium. The corresponding uranocene shows the methyl resonance only at $\delta + 15$ ppm; that is, in this compound the methyl group is locked into the *exo*-position.

The proton nmr resonances of several aryluranocenes are summarized in Table IV. It is especially noteworthy that the range of the [8]annulene resonances in phenyluranocene is rather small and reminiscent of the pattern found above for the isopropyl substituent (Fig. 4). According to the steric argument deduced above, this result suggests that the phenyl group, although undoubtedly twisted with respect to the [8]annulene ring, does not interact importantly with the opposite 8-membered ring and probably involves a phenyl-C_8 bond essentially coplanar with the C_8 ring. The *o*-tolyl group fits this same pattern and suggests strongly that with an *exo*-orientation of the *ortho*-methyl the interaction with the opposite ring is minimal.

The mesityl group is dramatic in its contrast. At 30 °C the range of C_8 proton chemical shifts is over 40 ppm. Yet, the weighted average of these shifts, −37.5 ppm, differs little from that of the other aryl substituents or of uranocene itself. This result must mean that the net amount of spin in the C_8

TABLE IV. ${}^1H$ Chemical Shifts of C_8 Protons of 1,1′-diaryluranocenes (δ, TMS, 30 °C).

H		−36.6		
Phenyl	−34.4	−36.2	−36.5	−37.1(H5)
p-$Me_2NC_6H_4$	−34.3	−36.2	−36.5	−37.1(H5)
o-Tolyl	−33.3	−34.2	−37.1	−38.8(H5)
Mesityl	−15.0(H2)	−33.2(H3)	−54.3(H4)	−57.3(H5)

ring is unchanged but that its distribution has changed markedly; that is, the uranocene structure with parallel rings and centrosymmetric metal is still retained. The obvious conclusion that the mesityl group must be markedly bent away from the opposite ring finds support in molecular models. The upfield position of H5, identified by its relative intensity, brings to mind the similar but less marked pattern for the t-butyl substituent. Indeed, the total pattern of C_8 ring hydrogen chemical shifts is similar to that of the t-butyl compound.

For most uranocenes the proton resonances are too broad for application of normal decoupling techniques. In the case of *25*, however, spin decoupling could be applied. Irradiation of one hydrogen position caused a sharpening of the resonances of adjacent protons. All of the ring positions could be assigned directly (Table IV) and are found to be in the t-butyl pattern.

As an nmr sample of *25* is cooled the resonances at first all show normal 1/T behavior. Below about −30 °C, however, H2, H3 and H4 show typical coalescence behavior, first broadening and fading into the baseline, and, below about −100 °C reemerge as pairs of peaks which again show linear 1/T dependence. This behavior is summarized in Fig. 5. Note that H5 remains sharp and normal throughout this entire range. Clearly, some dynamical process is involved. The most reasonable such process is based on a ground state conformation in which the two mesityl rings are close to each other as diagrammed in the structural representation shown for *25*. This structure is chiral and we suggest that the dynamical process involved above is a rotation about the ring axis that interconverts the R- and S-enantiomers. All seven ring hydrogens on each C_8 ring are distinct but the rotation interconverts the pairs 2 and 8, 3 and 7, 4 and 6. The two aryl rings are held together presumably by van der Waals forces. The magnitude of this interaction was determined by line shape analysis of the coalescing bands. Several rate constants were obtained and used to determine the activation parameters $\Delta H^{\ddagger} = 9.9$ Kcal mol^{-1} and $\Delta S^{\ddagger} = 11.3$ e.u. The positive entropy is consistent with the proposed process but the enthalpy value found is surprisingly high for the aryl ring–ring interaction. This result suggests that related studies could prove useful in determining such interaction parameters for other systems. Again, the wide range of chemical shifts and the symmetry of the uranocene system are singularly effective for such applications. A schematic representation of the potential surface for rotation about the uranocene ring axis is shown in Fig. 6.

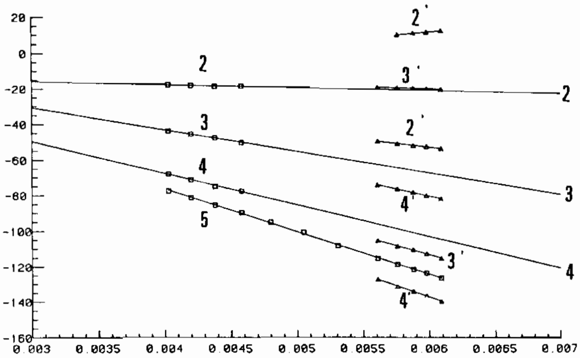

Fig. 5. δ *vs.* 1/T for 1,1′-dimesityluranocene.

A conclusive demonstration that the dynamical process involves interaction between the two mesityl rings is found in an equilibration experiment similar to that discussed above between *4* and uranocene. Addition of cyclooctatetraene dianion to *25* gave some uranocene together with the mixed ring system, mesityluranocene, *26*. The nmr spectrum of *26* showed no coalescence even down to −109 °C. Moreover, the fact that all three uranocene systems were present means that the equilibrium constant cannot differ in magnitude much from unity. Thus, the attraction between the aryl rings in *25* must be comparable to the steric strain involved between one mesityl ring and the opposite C_8 ring. In the ring rotation process, of course, the strain effect is approximately constant.

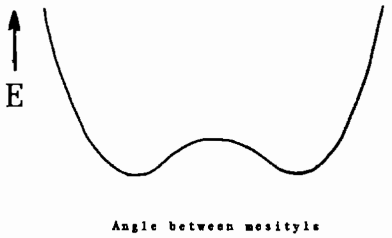

Fig. 6. Schematic diagram of potential surface for rotation about ring axis in *25*. Height of barrier is 9.9 Kcal mol^{-1}.

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