

1,1'-Dimesityluranocene and its unusual dynamic NMR phenomena [☆]

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Abstract

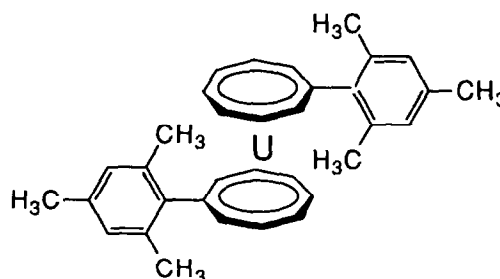
1,1'-Dimesityluranocene gives a ¹H NMR spectrum showing the mesityl groups in a locked position as expected with *exo*- and *endo*-*ortho*-methyl groups. The [8]annulene ring protons give four resonances at room temperature in a 2:2:2:1 ratio, but at low temperatures three of these resonances coalesce and reappear as six resonances at still lower temperatures. These results are interpreted in terms of two lowest energy enantiomeric structures in which the two mesityl groups are oriented close to each other, presumably held by van der Waals attraction. Separation with interconversion of the enantiomers involves a barrier of about 10 kcal mol⁻¹ but is rapid on the NMR time-scale at room temperature.

Keywords: Uranium; Uranocene; Dynamic NMR spectroscopy; Cyclooctatetraene; Actinide

1. Introduction

A number of substituted uranocenes have been described in previous papers [1–14] and have been reviewed [15–17]. Their properties suggested that the mesityl substituent would have unusual interest. The X-ray structure of 1,1',3,3',5,5',7,7'-octaphenyluranocene shows the phenyl groups to be twisted with respect to the [8]annulene rings [5] and the compound is remarkably air stable [4]. In 1,1'-di-*o*-tolyluranocene, the *ortho*-methyl groups are locked in the *exo* positions [14]. Thus, the mesityl substituent is expected to have a locked conformation with the *ortho*-methyl groups fixed in *exo* and *endo* orientations. Models show that in such a structure the *endo*-methyls interact significantly with the opposite [8]annulene ring. Available crystal structures of uranocenes show the central uranium to be fixed between the centers of two planar and parallel [8]annulene rings even in unsymmetrical cases [7,10,12]. Mesityl substituents would be expected to provide an important further test of this generalization. Accord-

ingly, 1,1'-dimesityluranocene (**1**) was prepared and in the event was found to have unexpected and significant NMR properties.



2. Results and discussion

Mesitylcyclooctatetraene (**2**) has been reported in minute yield from the Cope reaction [18] of mesityllithium with cyclooctatetraene [19]. In our hands, however, this method did not give useful yields. Instead, **2** was prepared in fair yield (42%) from the nickel(II) phosphine-mediated coupling reaction [20–23] of mesitylmagnesium bromide with bromocyclooctate-

[☆] Dedicated to Professor Herbert Schumann on the occasion of his 60th birthday.

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traene. Reduction of **2** with potassium in THF gave the dianion, which was then treated with uranium tetrachloride to give the uranocene **1** as a green solid characterized by its visible and mass spectra and combustion analysis. The corresponding thorocene was prepared by an analogous procedure.

3. NMR analysis

The proton NMR spectrum was as expected for the methyl groups of the mesityl rings. Since uranocenes are paramagnetic, various protons are subject to large shifts [24]; however, only pseudo-contact shifts are expected to be important for the twisted mesityl rings. For example, the *para*-methyl group is essentially normal at δ 0.8 ppm (30°C), since these protons are far from the uranium. The *exo*-methyl group is far downfield at 24.2 ppm. For comparison, the methyl protons of 1,1'-di-*o*-tolyluranocene (**3**) resonate at 17.1 ppm. [14], suggesting that the mesityl group is more twisted than the *o*-tolyl group from the [8]annulene plane. The other *ortho*-methyl group of the mesityl substituent resonates far upfield at -46.2 ppm. Similarly, the other *meta*-ring protons can be assigned at 11 (*exo*) and -1.2 (*endo*) ppm. The magic angle passes through the aryl ring and results in these large and opposite shifts.

The chemical shifts of the [8]annulene protons were surprising. In other substituted uranocenes the ring protons resonate typically in the region from about -30 to -40 ppm [24]. In aryluranocenes, however, the range is usually much less. The [8]annulene protons in 1,1'-diphenyluranocene, for example, resonate from -34 to -37 ppm [14,24]. In **1** these protons appear at -15 to -57 ppm! This is the largest spread that we have observed in such substituted uranocenes. Moreover, in other uranocenes these ring protons are relatively broad because of the paramagnetism and spin-spin splitting is not measurable, but in **1** it was possible to observe such splitting and to carry out normal spin decoupling experiments. These ring protons could thus be assigned unambiguously: -15.0 (2,8), -33.2 (3,7), -50.3 (4,6) and -57.3 (5). The pattern of these shifts is the same as in 1,1'-di-*t*-butyluranocene, in which the *t*-butyl groups may be bent away from the uranium [24]. The wider range in **1** suggests that any such bending away of the mesityl substituents is substantially greater than in the *t*-butyl case. The sharper ring resonances also suggest a greater ring-uranium distance, but any such change must be small; the uranium is still probably centrosymmetric between two parallel [8]annulene rings because the average chemical shift in **1**, -36.4 , is close to that of diphenyluranocene, -35.4 [14], and di-*t*-butyluranocene, -37.0 [24].

As an NMR sample in THF- d_8 was cooled, the resonances for the *exo*- and *endo-ortho*-methyls and

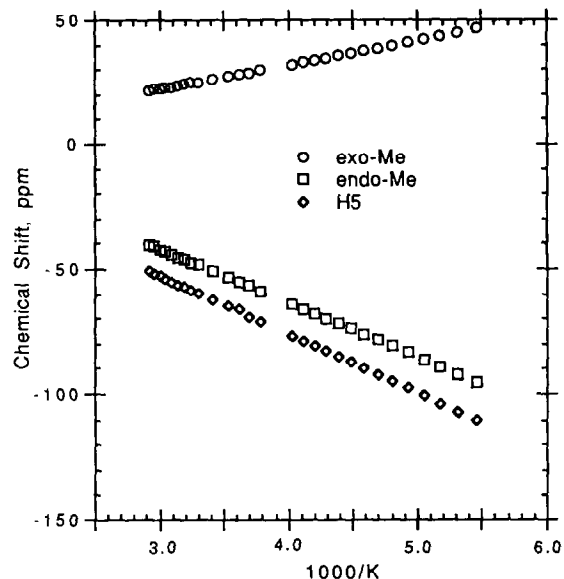


Fig. 1. Chemical shifts of resonances that show no coalescence as a function of $1/T$. Linear correlations of the data are as follows: *exo*-Me, $\delta = -6.698 + 9711/T$; *endo*-Me, $\delta = 23.178 - 21682/T$ and H(5), $\delta = 17.713 - 23462/T$. All $R = 0.9999$.

that for the ring-5 position showed normal linear $1/T$ dependence, as shown in Fig. 1. The other ring positions, however, gave a linear $1/T$ dependence at the higher temperatures but as the temperature was lowered these ^1H NMR resonances broadened and by -70°C had merged into the background. At lower temperatures they reappeared as six peaks that sharpened as the

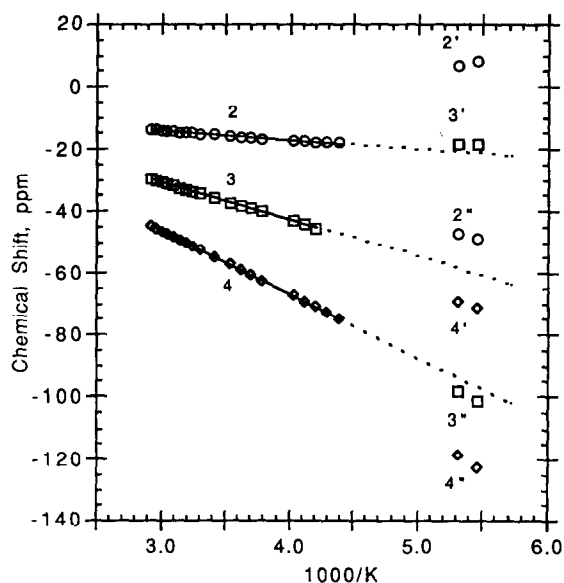
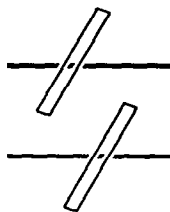


Fig. 2. Chemical shifts of coalescing protons as a function of $1/T$. The lines shown are as follows: 2, $\delta = -5.495 - 2911.6/T$ ($R = 0.994$); 3, $\delta = 5.396 - 12065/T$ ($R = 0.9998$); and 4, $\delta = 15.291 - 20532/T$ ($R = 0.9999$). Dotted lines show the extrapolations of the high-temperature lines through the coalescence region and into the slow exchange region.

temperature was lowered still more (Fig. 2). Thus, at low temperature the seven ring protons on each [8]annulene ring are non-equivalent but three pairs become dynamically equivalent at higher temperature. We interpret these results in terms of a low-temperature conformation in which the two mesityl rings are held close together. Models suggest the structure shown schematically as **1a** in which the *endo*-methyl of one mesityl is close to the benzene ring of the second mesityl, perhaps held by van der Waals or polarization forces; that is, this structure with the two mesityl rings close to each other is substantially more stable than the conformation shown as **1**. The low-temperature conformation of **1** is that of an enantiomer. We note that the tolyl analog **3** does not show this temperature behavior; hence the effect is not just between benzene rings. At higher temperatures the association between mesityls is broken and rotation of the [8]annulene rings occurs about the ring–uranium axis to give the other enantiomer. At higher temperatures this equilibration is fast on the NMR time-scale and renders three pairs of ring protons equivalent.



The low-temperature resonances were assigned as follows. Plots of the chemical shifts of the 2-, 3- and 4-ring protons vs. $1/T$ gave three lines at -25 to -55°C , as shown in Fig. 2. These lines were extrapolated (dotted lines in Fig. 2) into the low-temperature region. The averages of the pairs assigned in Fig. 2 correspond to the extrapolated lines. For example, at -90°C the extrapolated chemical shift and the average of the two assignments are, respectively, 2-, -21.4 , -20.1 ; 3-, -60.5 , -60.05 ; and 4-, -96.8 , -97.05 . A closely similar behavior was observed in toluene- d_8 and led to corresponding assignments [25]. These assignments provided the necessary parameters to apply the Nicolet NMR exchange simulation program for computer simulation of the spectra at -25 , -35 , -45 and -55°C to give the kinetic parameters in Table 1. These rates correspond to activation parameters of $\Delta H^\ddagger = 9.9 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = 11.3 \pm 2 \text{ eu}$. These values are consistent with the ΔG^\ddagger values that can be determined simply from the approximate coalescence temperatures. The positive entropy of activation is in agreement with the hypothesis since the mesityl groups have greater freedom of motion when not bonded to each

Table 1

Rate constants for equilibration of [8]annulene ring protons in **1** from computer simulation of NMR spectra

Temperature ($^\circ\text{C}$)	$k \times 10^5 \text{ (s}^{-1}\text{)}$
-25	33
-35	12.5
-45	5.0
-55	1.85

other. The magnitude of the enthalpy of the association of about 10 kcal mol^{-1} , however, is surprisingly high.

Another experiment confirmed that a cooperative phenomenon between the two mesityl groups is responsible. 1-Mesityluranocene (**4**) was prepared by equilibrating **1** with cyclooctatetraene dianion in THF solution to give a mixture of the two compounds together with a small amount of uranocene. This mixture of the three compounds was then cooled in the probe of an NMR instrument. The spectrum assigned to **4** showed no such coalescence, even down to -109°C (the freezing point of the solvent).

4. Conclusions

The stable structure of **1** is that in which the two mesityl rings are held close to each other, presumably by van der Waals attraction. Separation of the two rings by rotation about the ring-centroid–uranium axis involves a surprisingly high barrier of about 10 kcal mol^{-1} and results in interconversion of two enantiomers.

5. Experimental

5.1. Mesitylcyclooctatetraene, **2**

To a flame-dried 250 ml three-necked flask equipped with a condenser and dropping funnel and containing 1 g (42 mmol) of magnesium turnings and 5 ml of dry diethyl ether was added slowly under argon 6 g (30 mmol) of bromomesitylene in 15 ml of dry diethyl ether. The mixture was stirred for 4 h and became dark with partial disappearance of the magnesium. In a separate flask were mixed 5.5 g (30 mmol) of bromocyclooctatetraene [26] and 0.185 g (0.3 mmol) of bis(triphenylphosphine)nickel chloride [27] in 50 ml of dry diethyl ether under argon. To this mixture was slowly added the Grignard solution by syringe. The reaction was initially exothermic and became red–brown. A white precipitate was observed after the solution had been stirred for 24 h, at which time the reaction was quenched by adding 20 ml of saturated aqueous ammonium chloride. The layers were separated and the or-

ganic phase was washed once with 40 ml of water followed by 40 ml of brine. The yellow solution was dried over MgSO_4 , evaporated and the residue was distilled. There was a substantial forerun, which consisted of mesitylene and bromocyclooctatetraene, b.p. 30–40°C (2 mmHg), then **2** was obtained as a yellow oil, b.p. 126–128°C (2 mmHg), (lit. b.p. 95°C at 0.05 mmHg) [19], 2.8 g (42%). ^1H NMR, δ (ppm): 6.80 (s, 2H), 5.85 (m, 7H), 2.23 (s, 5H), 5.68 (m, 1H), 2.23 (s, 3H), 2.19 (s, 6H). Note that the small difference between the *ortho*- and *para*-methyls is typical of other vinylmesitylenes [28]. Mass spectrum, m/z (relative intensity (%)): 222 (M^+ , 95.88), 207 (100.00), 192 (59.50). ^{13}C NMR (25 MHz), δ (ppm): 142.9, 138.6, 135.3, 132.6, 131.7, 128.6, 128.0, 20.8, 20.1. Anal. Calc. for $\text{C}_{17}\text{H}_{18}$: C, 91.84; H, 8.16. Found: C, 90.57; H, 8.00%.

5.2. 1,1'-Dimesityluranocene, **1**

To a solution of 1.11 g (5 mmol) of **2** in 110 ml of dry THF in an argon-filled glove-box was added 0.39 g (10 mmol) of clean potassium. The mixture was stirred for 20 h, after which time all of the potassium had disappeared, leaving an opaque brown solution. ^1H NMR spectrum of a THF- d_8 solution of **2** dianion, δ (ppm): 6.77 (s, 2H), 5.77 (m, 5H), 5.56 (m, 2H), 2.28 (s, 3H), 2.14 (s, 6H); ^{13}C , 135.6, 130.6, 127.8, 127.0, 90.8, 90.1, 89.7, 89.2, 88.9, 20.9, 20.2. Note that $\Delta\delta$ for the ^1H chemical shifts of the *ortho*- and *para*-methyls, 0.13 ppm, is much lower than that normally characteristic of a mesityl group attached to an aromatic ring (e.g. phenylmesitylene); by this criterion, cyclooctatetraene dianion would not be regarded as aromatic [28–32].

To the solution of the dianion was added a solution of 0.93 g (2.5 mmol) of uranium tetrachloride in 40 ml of THF. The mixture turned dark green and was stirred for 4 h. The THF was removed by vacuum transfer and the residue was Soxhlet extracted for 14 h with hexane. The hexane was removed by vacuum transfer, affording 1.2 g (71% yield) of a green solid, m.p. 280°C. ^1H NMR (toluene- d_8 , 90 MHz, 30°C), δ (ppm): 24.2 (s, 3H, *exo*-Me), 11.0 (s, 1H, H-3'), 0.8 (s, 3H, *p*-Me), -1.2 (s, 1H, H-5'), -15.0 (d, $J = 10$ Hz, 2H, H-2), -33.3 (broad t, 2H, H-3), -46.2 (s, 3H, *endo*-Me), -50.3 (broad t, 2H, H-4), -50.7 (broad t, 1H, H-5). NMR assignments of the COT ring protons was done with decoupling experiments and observing sharpening of some resonances when others were irradiated. Mass spectrum, m/z (relative intensity (%)): 682 (46.31), 400 (58.18), 461 (10.79), 222 (93.97), 207 (100.00), 192 (62.05). Visible spectrum, λ_{max} (nm): 609, 639, 662. A small amount of the material was recrystallized from THF–hexane for analysis. Anal. Calc. for

$\text{C}_{34}\text{H}_{36}\text{U}$: C, 59.82; H, 5.28. Found: C, 59.72, H, 5.41%.

5.3. 1,1'-Dimesitylthorocene

A similar procedure was used with 0.5 g (2.3 mmol) of **2**, 0.175 g (4.5 mmol) of potassium and 0.42 g (1.13 mmol) of thorium tetrachloride to give 0.5 g (65% yield) of a yellow solid. ^1H NMR, δ (ppm): 7.15 (m), 6.3 (m), 6.85 (m), 2.80 (s, *p*-Me), 2.45 (s, probably *exo*-*o*-Me), 1.5 (s, probably *endo*-*o*-Me). Note that δ (*p*-Me – *exo*-*o*-Me) = 0.35 ppm is comparable to those for arylmesitylenes and that the thorocene ring system by Musso's criterion [28–32] would be regarded as aromatic. Mass spectrum, m/z (relative intensity (%)): 676 (13.34), 677 (4.64), 222 (89.98), 207 (100.00), 192 (85.84). Anal. Calc. for $\text{C}_{34}\text{H}_{36}\text{Th}$: C, 60.34; H, 5.36. Found: C, 60.63, H, 6.20%.

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