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[1,5-Bis-[8]annulenylpentane]uranium and [1,2-Bis-([8]annulenyldimethylsilyl)ethane]uranium, the First Bridged Uranocenes

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[1,5-Bis-[8]annulenylpentane]uranium and [1,2-Bis-([8]annulenyldimethylsilyl)ethane]uranium, the First Bridged Uranocenes

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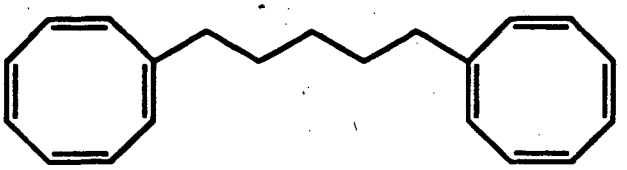
Contribution from the Department of Chemistry, University of California, and the Lawrence Berkeley Laboratory, Berkeley CA 94720

Abstract: Methods have been developed for the efficient preparation of some chains substituted with cyclooctatetraene groups at both ends. The titled compounds **3** and **4** could be prepared and characterized. The temperature dependent NMR spectrum of the bridged uranocene **4** indicates a flexible molecule that twists between enantiomeric structures with a barrier of about 13 Kcal mol^{-1}.

Bridged ferrocenes in which the two ligand rings are joined by a tether were prepared not long after the first preparation of the parent molecule.[2] By contrast, although many uranocenes and related actinide sandwich compounds have been prepared since 1968[3] no bridged uranocene-type structure has been reported. In part this is no doubt due to the greater difficulty in obtaining suitable ligands. Chains containing two cyclooctatetraene (COT) rings have only recently been reported.[4] We report here some of our studies in this area; we present syntheses of the di-COT compounds **1** and **2** and illustrate their conversion to bridged uranocenes.



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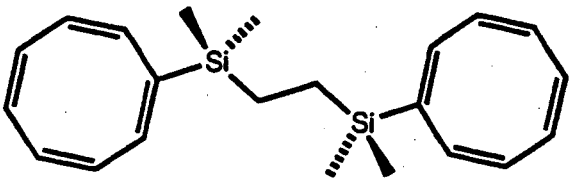


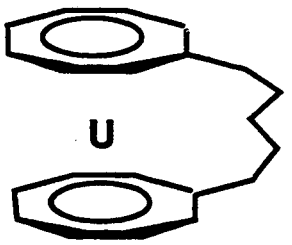
2

The preparation of monosubstituted cyclooctatetraenes has been the subject of various studies.[5] The most general methods involve cuprate reactions with bromocyclooctatetraene,[6] COTBr, or alkylation of an organometallic derivative of cyclooctatetraenyl carbanion with a suitable electrophile. The latter method was used in the present work. Various methods for the generation of the carbanion have been used but the simplest appears to be that of metal/halogen exchange using COTBr and an alkyllithium. A major source of problems in COT chemistry is that of polymerisation. In the syntheses described here these polymerisation problems are doubled since the alkylation step has to be carried out twice.

For the synthesis of the bis-cyclooctatetraenyl compound **1** we attempted the direct alkylation of cyclooctatetraenyllithium, generated by Br/Li exchange from the bromide and *n*-butyllithium, with 1,5-dibromopropane. The product mixture contained large amounts of *n*-butylcyclooctatetraene which undoubtedly arose from the reaction of cyclooctatetraenyllithium with the *n*-butyl bromide formed in the exchange reaction. The use of *t*-butyllithium circumvented this alkylation problem. Treatment of COTBr with 80% of the theoretical quantity of *t*-butyllithium followed by the dibromide produced **1** in 70% overall yield. In a similar manner 1,2-bis-(cyclooctatetraenyldimethylsilyl)ethane **2** was formed (45%) by the alkylation of cyclooctatetraenyllithium with 1,2-bis-(chlorodimethylsilyl)ethane. Again, the use of *t*-butyllithium for the exchange afforded a cleaner product. Satisfactory micro-analytical data were obtained for the ligands prepared above. This process for the preparation of linked cyclooctatetraenyl compounds is probably generally applicable.

Conversion of the ligands to the corresponding bridged uranocenes was accomplished by straighforward analogy to simple uranocenes. Treatment of 1,5-dicyclooctatetraenylpentane **1** with an excess of metallic potassium and uranium tetrachloride in THF produced a green hexane-soluble product for which the EI mass spectrum shows a peak at m/Z 514 which corresponds to the molecular ion for the proposed structure **3**. No peaks above this value were obtained indicating that dimeric and polymeric structures are not present. A fragment peak at m/Z 446 is in agreement with the gross structure $(C_8H_8)U^+$ which is often observed for alkyluranocenes where the alkyl groups are stripped off by electron impact. Although this compound could be partially characterized a pure sample could not be obtained. All attempts to produce crystals suitable for X-ray structure determination proved futile. The visible spectrum exhibits a typical uranocene-like spectrum in the 600-700 nm range. The most intense band at 614 nm is similar to that of 1,1'-diethyluranocene, 619 nm,[7] but the cascade of four bands was compressed (614-640 nm) compared to the diethyl compound (619-682 nm).[7] The comparison of the ^1H NMR spectrum with that of other uranocenes is instructive. The α-methylene protons of **3** at δ = -20 ppm are similar to those of the α-methylenes of 1,1'-diethyluranocene, -17 ppm, and of 1,1'-di-n-butyluranocene, -19 ppm,[8] suggesting that the average conformation of these methylene groups is about the same in the three compounds. On the other hand, the central methylene group of **3** at δ = -30 ppm is far upfield of the comparable methylene group of 1,1'-di-n-butyluranocene, δ = 1.[8] This result is consistent with dipolar shifts found for substituted uranocenes; in general, hydrogens exo with respect to the ring planes and the uranium have downfield shifts whereas endo hydrogens are upfield. One significant difference concerns the ring protons. In **3**, they show the 2:2:2:1 pattern typical of bulky substituents such as t-butyl rather than the 2:1:2:2 pattern given by ethyl and n-butyl

substituents; that is, the 5-proton is the furthest upfield in **3** unlike that of n-alkyl substituted uranocenes.[8]



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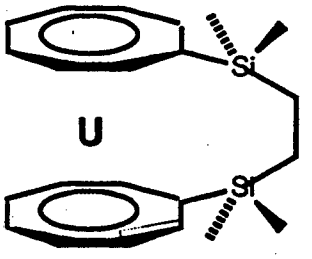

4

The corresponding reaction of the silicon compound **2** was more facile; reaction with metallic potassium occurred readily to give a brown suspension of the tetraanion, which on treatment with one equivalent of uranium tetrachloride produced a green hexane-soluble solid product whose properties are consistent with **4**. This material could be sublimed at relatively low temperatures (130 °C, 10^{-3} mbar) and could be more fully characterized. The mass spectrum shows a molecular ion at m/Z 588 which is the base peak and there were no peaks corresponding to dimeric or polymeric structures. The HRMS is consistent with the proposed molecular formula $C_{22}H_{30}Si_2U$. The silyl complex appears to be more stable than the carbon analog **3**.

The NMR spectrum of **4** is also typical of uranocenes.[8] In particular, the paramagnetically shifted ring hydrogens are similar to those of 1,1'-bis-(trimethylsilyl)uranocene,[9] with the 5-hydrogen furthest upfield. The methyl groups at δ = -3 ppm are somewhat downfield from those of the trimethylsilyl substituent, consistent with the average exo-like position of the two methyls groups in **4**. The methylene groups in **4**, in contrast, are located far upfield at -21 ppm consistent with their endo-like conformation. The NMR spectrum was also run at low temperatures and showed several features of interest. As shown in Figure 1 the isotropic shifts of several of the protons showed a typical linear dependence on 1/T in common with most uranocene protons.[8] Isotropic shifts for a number of uranocenes have been

determined used the corresponding thorocenes as diamagnetic analogs.[8] For **4** we used the recently published data for 1,1',4,4'-tetrakis-(trimethylsilyl)thorocene[10] in which the methyl protons have $\delta = 0.58$ and the ring protons 6.70 and 6.90 ppm. Accordingly for **4** we estimated the diamagnetic δ to be 0.6 for the hydrogens adjacent to the silicon and 6.7, 6.9, 6.9 and 6.9 ppm for the 2-, 3-, 4-, and 5-COT ring positions, respectively. Reasonable changes in these numbers do not affect the results. The isotropic shifts for the 5-COT proton show a slight curvature with 1/T (Figure 2). Except for the COT-5 proton, the NMR spectra show the coalescence behavior at low temperature typical of dynamic NMR systems. A reasonable explanation is given by a structural model of **4**, shown as **5** in Figure 3. Using standard bond distances and angles the compound probably has C_2 symmetry; Figure 3 therefore represents one enantiomer and at normal temperatures the compound twists about the methylene groups to interconvert enantiomers at rates fast compared to the NMR time scale. For each enantiomer the two methyls on the silicon, the two methylene hydrogens (shown as H_x (exo) and H_e (endo) in Figure 3), and the pairs of ring protons, 2- and 8-, 3- and 7-, 4- and 6-, are magnetically different. Unfortunately, we could not get measurements at low enough temperature to see the "frozen" states, but it is possible to get a rough measure of the barrier.

The COT-2 and COT-3 protons have coalesced by -52 °C and the COT-4 proton by -38 °C. At coalescence the rate constant for interconversion between two states is of the order of magnitude of the chemical shift difference between the corresponding pairs. Considering the total range of chemical shifts of the ring protons, about 10 ppm, the shift differences between pairs such as 2- and 8- and between 3- and 7- are expected to be of the order of magnitude of 1 ppm. Thus, $\Delta G^{\ddagger}$ is about 13 Kcal mole^{-1}. For the methyl and methylene protons the chemical shift differences are an order of magnitude greater and the coalescence temperatures are correspondingly higher. The interconversion of the enantiomers is difficult to

accomplish with models and requires substantial spreading apart of the rings; thus, the barrier for interconversion is relatively high.

Experimental Section

1,5-Bis-cyclooctatetraenylpentane, 1. To 7.7 g (42.5 mmol) of bromocyclooctatetraene[11] in 50 mL of THF at -60 °C under Ar was added 50 mL of 7M *t*-butyllithium (85 mmol) over 45 min. The solution turned from orange to dark green. After stirring for 30 min, 2.6 g of 1,5-dibromopentane was added dropwise under Ar over 20 min. The mixture was allowed to warm slowly to room temperature. After 36 h the mixture was quenched at 0 °C with 20 mL of sat. aq. NH_4Cl and extracted with hexane. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* at room temperature and chromatographed on a short basic alumina column with hexane followed by preparative tlc on silica with hexane to yield 1.92 g (70%) of **1**; mass spectrum, m/Z 276; ^1H NMR ($CDCl_3$) δ 5.7 (br, 14H, COT), 2.0 (t, 4H), 1.4 (m, 6H). Anal. Calcd. for $C_{21}H_{24}$: C, 91.19; H, 8.81. Found: C, 90.89; H, 8.77.

η^{16}-(1,5-Bis-([8]-annulenyl)pentane)uranium(IV), 3. To a solution of 500 mg. (1.8 mmol) of **1** in 50 mL of THF was added 509 mg (13 mmol) of potassium. After stirring overnight, the brown mixture was filtered and to the solution was added 1.3 g (3.4 mmol) of UCl_4. After stirring for 48 h the mixture was filtered and the solvent was removed under vacuum. The residue was stirred with toluene to remove the excess UCl_4. The mixture was filtered and the solvent was removed under vacuum to leave 416 mg (45%) of green solid. The product could not be recrystallized or sublimed. The crude product was characterized by NMR and mass spectroscopy; M.S. m/Z 514 (M^+, 35.9%); 515 ($(M+1)^+$, 7.6%); 91 (100%); UV-vis, 614, 625, 634, 640 nm.; ^1H NMR (THF-d_8, 22 °C), -20.14 (s, 4H, alkyl), -20.29 (s, 4H, alkyl), -30.03 (s, 2H, alkyl), -33.80 (s, 4H, COT ring), -34.06 (s, 2H, alkyl), -35.00 (br s, 2H, alkyl), -37.26 (br s, 4H, COT ring), -41.03 (br s, 4H, COT ring), -46.14 (br s, 2H, COT-5).

1,2-Bis-(cyclooctatetraenyldimethylsilyl)ethane, 2. To 6 g (33 mol) of bromocyclooctatetraene in 50 mL of THF at -75 °C was added 35 mL of *t*-butyllithium, 1.7M in pentane (65 mmol) over 1 h. The solution gradually turned orange brown and finally dark. The solution was stirred at -75 °C for 15 min and 1,2-bis(chlorodimethylsilyl)ethane (2.54 g; 11.8 mmol) in 15 mL of THF was added over a period of 1 h with vigorous stirring. The reaction mixture was allowed to warm to RT overnight. The red reaction mixture was quenched with aq. NH_4Cl and the organic layer was separated, poured into water, extracted with ethyl ether and dried over $MgSO_4$. After the removal of solvent the crude product was chromatographed on silica gel with hexane to give 1.86 g of **2** (45%) as a yellow viscous oil that crystallized slowly over several days. ^1H NMR ($CDCl_3$) 5.65-5.95 (m, 14 H, COT ring protons); 0.45 (br s, 4H, $-CH_2CH_2$); 0.04 (s, 12H, $-CH_3$). M.S. 350 (M^+, 3.37%). Anal. Calcd. for $C_{22}H_{30}Si_2$: C, 75.36; H, 8.62. Found: C, 75.71; H, 8.65.

η^{16}-(1,2-Bis-([8]-annulenyldimethylsilyl)ethane)uranium(IV), 4. To 248 mg of **2** (0.708 mmol) in 10 mL of THF was added 300 mg of potassium (7.69 mmol) with vigorous stirring. Stirring was continued for 20 h to give a brown solution. After filtration to remove the excess K the solution was added slowly (over 25 min.) with stirring to 380 mg of UCl_4 (1 mmol) in 10 mL of THF to give a green solution. After stirring for 5 h the THF was removed in vacuo to give a green solid which was extracted with hexane. Evaporation gave 291 mg (70%) of a green solid that sublimes at 10^{-3} mb/130 °C. ^1H NMR (THF-d_8, 22 °C) -3.485 (s, 12H, $-CH_3$); -21.145 (br.s., 4H, $-CH_2CH_2-$); -32.515 (br.s., 4H, COT ring protons); -36.769 (br.s., 4H, COT ring protons); -42.260 (b.s., 4H, COT ring protons); -42.751 (b.s., 2H, COT ring protons). M.S. (E.I.) 588 (M^+, 100%), 589 ($(M+1)^+$, 33.59%), 590 ($(M+2)^+$, 1.82%). Simulation for $C_{22}H_{30}Si_2U$: 588 (100%), 589 (34.6%), 590 (12.32%). HRMS. Calcd 588.2393(8). Found 588.2384.

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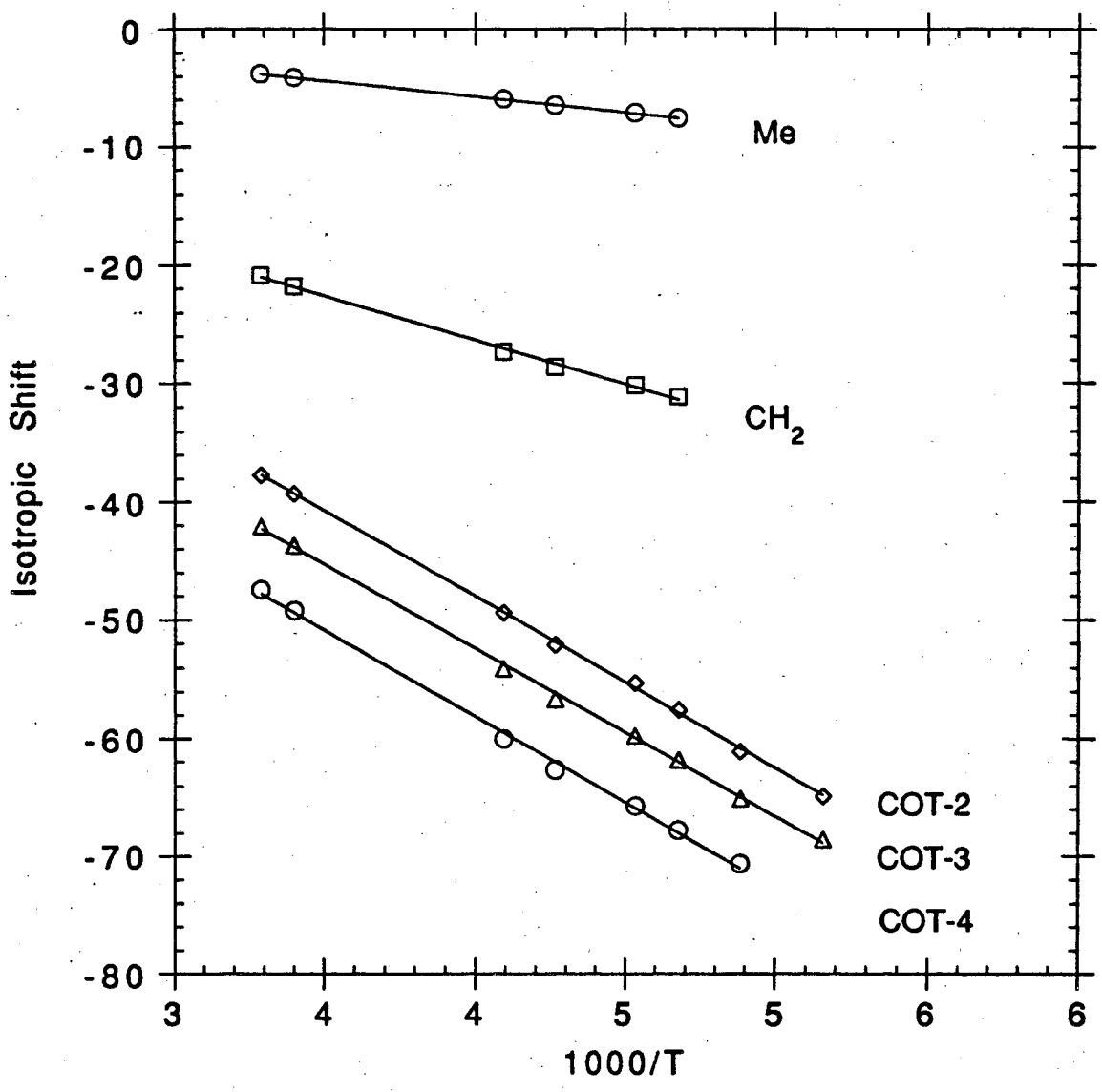

Figure 1. Isotropic shift of protons in **4**. Equations for the linear correlations are Me, δ_{ISO} = 5.078 - 2696.7/T (r=1.000); CH_2, δ_{ISO} = 3.622 - 7480.2/T (r=0.998); COT-2, δ_{ISO} = 10.101 - 14524/T (r = 1.000); COT-3, δ_{ISO} = 4.390 - 14195/T (r = 0.999); COT-4, δ_{ISO} = 0.165 - 14566/T (r = 0.999).

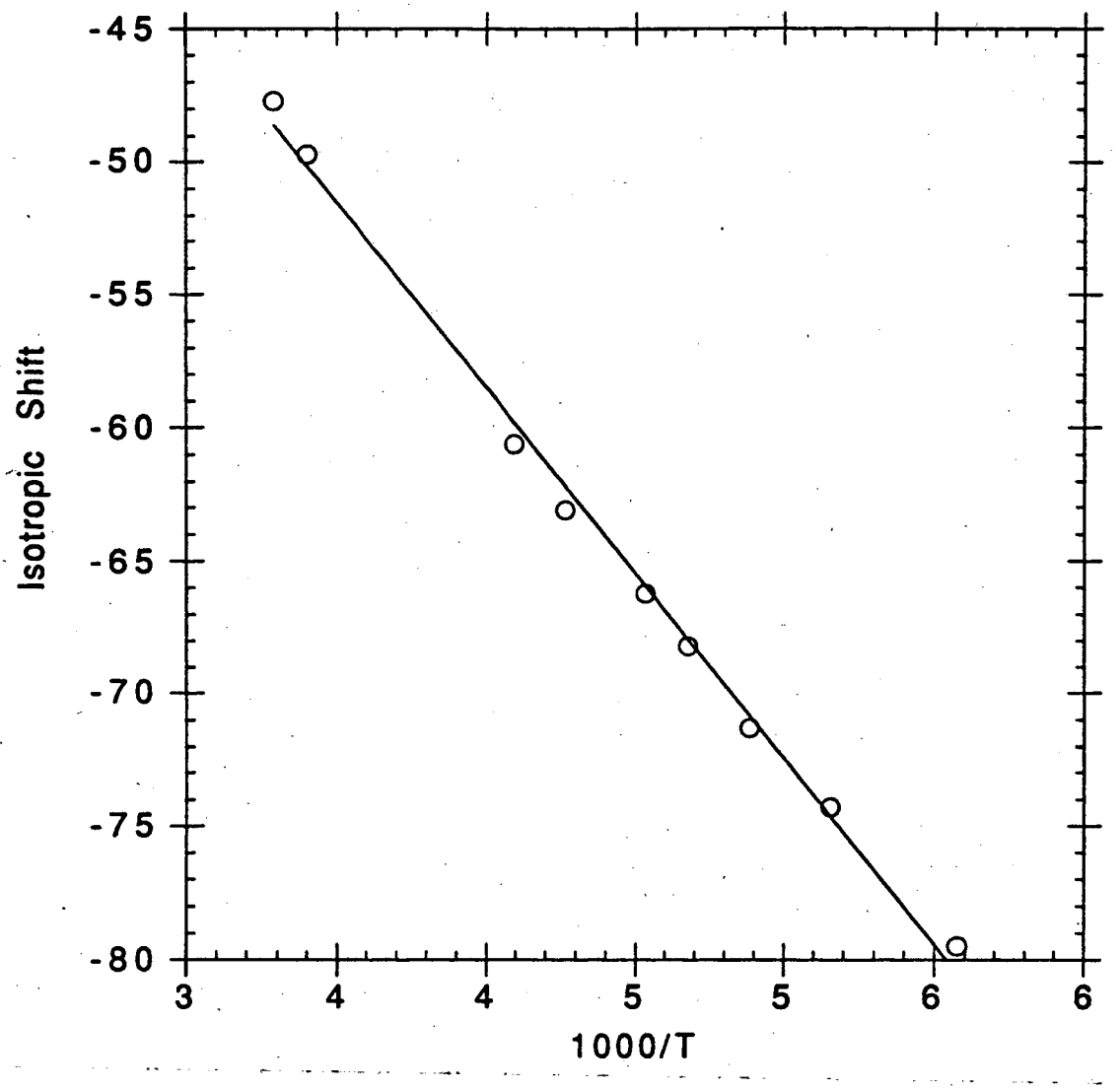

Figure 2. Isotropic shift of the COT-5 proton as a function of 1/T. The linear correlation shown is δ_{ISO} = -2.713 - 13950/T (r = 0.998).

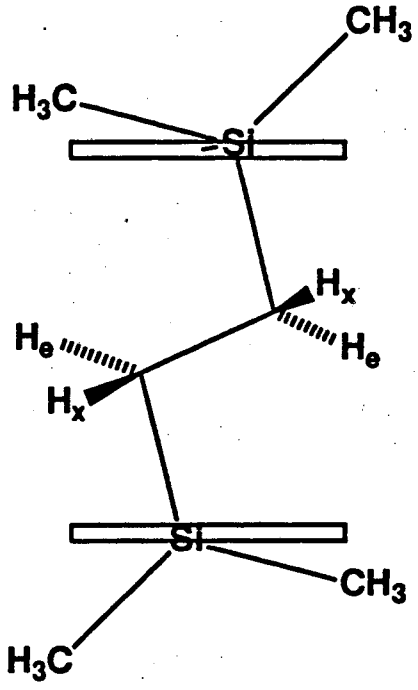

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Figure 3. One conformation of a structural model of **4** shown end on.

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[1] Present address: Dept of Chem, New Univ of Lisbon, 2825 Monte de Caparica, Portugal

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