*J. Org. Chem.* **1994,** *59,* 5516–5517

# Synthesis and Characterization of [6](9,10)Anthracenophane

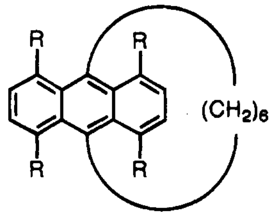
Yoshito Tobe*, Naoto Utsumi, Shinji Saiki, and Koichiro Naemura

*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan*

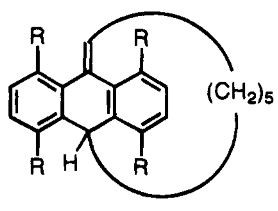
*Received June 27, 1994*⊗

*Summary:* Extremely air- and acid-sensitive [6](9,10)-anthracenophane (**1**), the smallest-9,10-bridged anthracene, has been synthesized by reductive deoxygenation of diepoxyanthracenophane (**4**) with a low-valent titanium reagent, and it was characterized by its NMR and electronic spectrum.

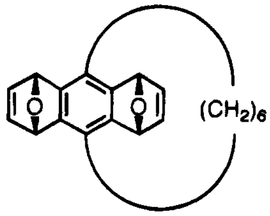
The chemistry of strained [$n$]paracyclophanes with short bridges has been extensively explored during the last decade.[1] By contrast, little has been learned about short-bridged [$n$](9,10)anthracenophanes, despite the fact that these molecules serve as suitable models to study the dependancy of aromaticity on structure deformations. The smallest known representative of this class had been the diketo derivatives of [8]anthracenophanes.[2] On the basis of MMX and AM1 calculations Rosenfeld predicted difficulties in synthesizing smaller [$n$](9,10)anthracenophanes with $n \leq 7$.[3] Namely, as the bridge becomes smaller, the methylenedihydroanthracene isomer becomes energetically more favorable. Recently, we succeeded in the synthesis, isolation, and structure determination of 1,4,5,8-tetramethyl[6](9,10)anthracenophane (**2**), a tetramethyl-substituted derivative of the smallest 9,10-bridged anthracene.[4] We achieved the synthesis of **2** by the bis-benzannelation methodology starting from a substrate already having the [6]paracyclophane substructure, taking into account the expected kinetic lability of short-bridged anthracenophanes. Even the tetramethyl derivative **2** was highly acid-sensitive, and it readily isomerized to methylenedihydroanthracene **3**. However, we were unable to detect the parent hydrocarbon **1** using reductive deoxygenation of diepoxyanthracenophane (**4**) with a low-valent titanium reagent, as employed for the synthesis of **2**. We obtained instead methylenedihydroanthracene **5** and dihydroanthracene **6** in a ratio of 1:2. Thus, it appears that without the tetramethyl protecting group, the reactive central ring of the anthracene core would not survive under the usual deoxygenation conditions. By modifying the reaction conditions and work-up procedures, we succeeded in the synthesis and characterization of the extremely air- and acid-sensitive hydrocarbon **1**.



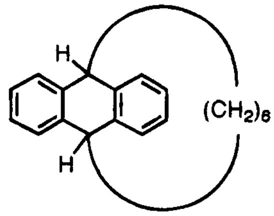
**1** R=H
**2** R=CH$_3$



**3** R=CH$_3$
**5** R=H



**4**



**6**

As reported previously, treatment of **4** with a low valent titanium reagent prepared from TiCl$_4$/LiAlH$_4$/Et$_3$N (7:2.5:1)[5] followed by aqueous workup furnished **5** and **6** in a 1:2 ratio.[4] In order to exclude air and acid, we used a large excess of Et$_3$N (25 equiv)[6] and worked up the reaction mixture by directly passing it through deactivated alumina (with 6% water) under nitrogen. Subsequent chromatography on deactivated alumina (with 15% water) under nitrogen afforded a hydrocarbon fraction as a yellow solid which was proved by the $^1$H and $^{13}$C NMR spectra as a 3:2 mixture of **1** and dihydroanthracene **6**.[7] Figure 1 shows the $^1$H NMR spectrum of the product in toluene-$d_8$ at −50 °C. The assignment of the signals was made on the basis of the 2D NMR and NOE experiments.[8] At this temperature, the flipping of the methylene bridge is frozen so that six kinds of the methylene signals (Ha–Hf) are discerned. The signal of the most shielded methylene protons (Hf) appears at $\delta$ −1.84; the chemical shift is similar to that of the corresponding protons of **2** ($\delta$ −1.81 in CD$_2$Cl$_2$).[4] The $^{13}$C NMR spectrum (−50 °C)[9] exhibited nine signals for **1** together with seven signals for **6**.[8] Treatment of the NMR sample with TFA resulted only in the disappearance of the signals of **1** probably because of its polymer-

---

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1994.

[1] For recent reviews: (a) Bickelhaupt, F.; de Wolf, W. H. *Recl. Trav. Chim. Pays-Bas* **1988,** *107,* 459. (b) Bickelhaupt, F. *Pure Appl. Chem.* **1990,** *62,* 373. (c) de Wolf, W. H.; Bickelhaupt, F. In *Advances in Strain in Organic Chemistry;* Halton, B., Ed.; JAI Press: Greenwich, CT; Vol. 3, p 185. (d) Kane, V. V.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron,* in press. (e) Tobe Y. In *Topics in Current Chemistry;* Weber, E., Ed.; Springer-Verlag: Heidelberg, in press.

[2] (a) Helder, R. Ph. D. Thesis, Rijksunversiteit te Groningen, 1974. (b) Rosenfeld, S. M.; Sanford, E. M. *Tetrahedron Lett.* **1987,** *28,* 4775. (c) Ohta, M.; Tamura, S.; Okajima, T.; Fukazawa, Y. 63rd Annual Meeting of the Chemical Society of Japan, March 28–31, 1992; Abstract No. 3B234.

[3] Rosenfeld, S.; Sheldow, A. M.; Kirwin, J. M.; Amaral, C. A. *J. Org. Chem.* **1990,** *55,* 1356. (b) Rosenfeld, S.; Shedlow, A. *J. Org. Chem.* **1991,** *56,* 2247. (c) Rosenfeld, S. *J. Org. Chem.* **1993,** *58,* 7572.

[4] Tobe, Y.; Ishii, H.; Saiki, S.; Kakiuchi, K.; Naemura, K. *J. Am. Chem. Soc.* **1993,** *115,* 11604.

[5] (a) Xing, Y. D.; Huang, N. Z. *J. Org. Chem.* **1982,** *47,* 140. (b) Wong, H. N. C. *Acc. Chem. Res.* **1989,** *22,* 145.

[6] By the use of a large excess of Et$_3$N, tetramethyl derivative **2** was obtained in 68% yield without any formation of its isomer **3** or the dihydro derivative.

[7] Hydrocarbon **1** is thermally stable but is very sensitive to air; on exposure of a solution containing **1** to air, the characteristic yellow color disappeared immediately leaving insoluble materials.

[8] The $^{13}$C NMR, $^1$H–$^1$H and $^1$H–$^{13}$C COSY, DNOE, and VT–$^1$H NMR spectra are listed in supplementary material.

[9] $^{13}$C NMR spectrum for **1**: $\delta$ 135.6 (s), 133.2 (s), 125.6 (d), 125.0 (d), 124.9 (d), 124.5 (d), 34.2 (t), 33.7 (t), 25.8 (t). The signals for the secondary and tertiary carbons which overlapped with the solvent peaks were found out by the DEPT experiments. One of the quaternary carbon signals of **1**, however, was not found.

0022-3263/94/1959-5516$04.50/0

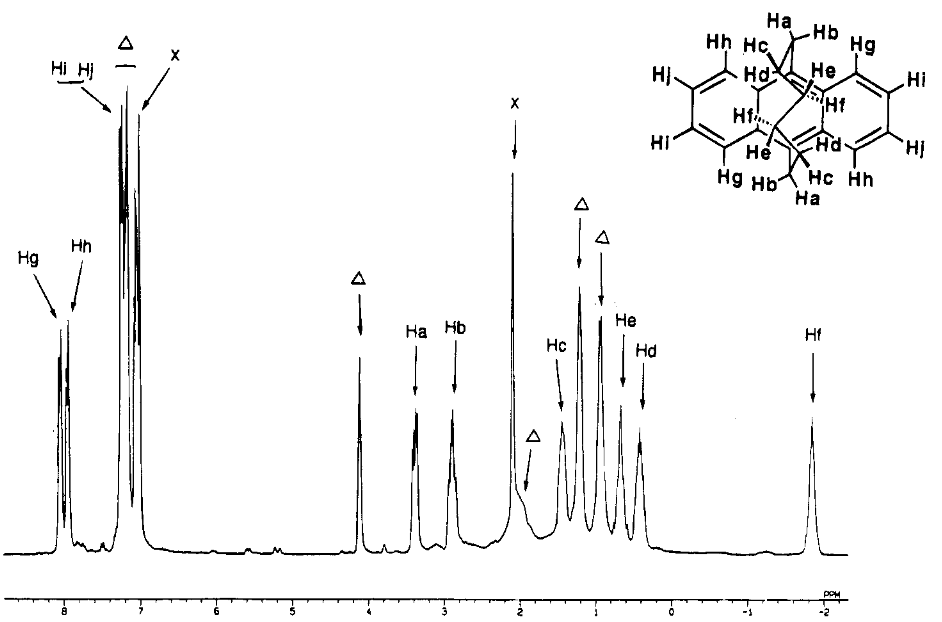
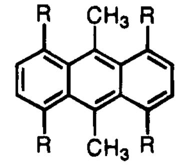


**Figure 1.** $^1$H NMR spectrum of a mixture of **1** and **6** (3:2) in toluene-$d_8$ at −50 °C. The signals marked by Δ and × are for **6** and the solvent, respectively.

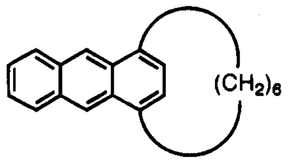
ization. However, treatment with silica gel under nitrogen yielded immediately a mixture of **5** and **6** (1:2).[10]

The electronic spectrum of the product containing **1** shows absorption maxima at 435, 415, and 392 (sh) nm (hexane) which are characteristic of the anthracene chromophore. The longest wavelength absorption of **1** exhibits a remarkable bathochromic shift in comparison with that of 9,10-dimethylanthracene (**7**: 398, 377, 358 nm), indicating a severe out-of-plane deformation of the anthracene ring in **1**. The bathochromic shift of the longest wavelength absorption of **1** (0.26 eV) relative to **7** is larger than that of **2** (0.19 eV)[4] relative to 1,4,5,8,9,10-hexamethylanthracene (**8**),[11] due to the distortion present in the latter reference compound **8**.

The $^1$H NMR spectrum of **1** is temperature dependent due to the flipping of the bridge; the signals observed at −50 °C for the aromatic protons Hg ($\delta$ 8.26) and Hh ($\delta$ 8.10) coalesced at −5 °C and appeared as a double doublet at 50 °C.[8] Decoupling by irradiation of the aromatic protons Hi and Hj (around $\delta$ 7.2) simplified the signals to a pair of singlets at −50 °C and a singlet at 50 °C. The exchange rates were estimated by line shape analysis using the DNMR2 program[12] to yield $\Delta G^{\ddagger}$(25 °C) of 13.7 kcal/mol for the flipping process. This is in the same range as that of [6](1,4)anthracenophane (**9**: 13.4 kcal/mol)[13] and [6]paracyclophanes (13−14 kcal/mol),[14] but is considerably larger than that of the tetramethyl derivative **2** (9.5 kcal/mol).[4] These results indicate that the out-of-plane deformation of the central aromatic ring of **1** is smaller than that of **2** as we predicted based on the AM1 calculations.[4] The larger distortion in **2** is, therefore, ascribed to the steric interaction between the methyl groups and the benzyl methylenes.



**7** R=H
**8** R=CH$_3$



**9**

**Supplementary Material Available:** Experimental procedures and copies of DNOE, $^{13}$C NMR, $^1$H−$^1$H and $^1$H−$^{13}$C COSY, and temperature dependent $^1$H NMR spectra (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(10) Approximately half of **1** was lost during silica gel-catalyzed isomerization of **1** to **5** probably by polymerization.

(11) Hart, H.; Nwokogu, G. *J. Org. Chem.* **1981**, *46*, 1251.

(12) We are indebted to Professors Y. Fukazawa and S. Usui of Hiroshima University for the PC version of this program.

(13) Tobe, Y.; Takahashi, T.; Ishikawa, T.; Yoshimura, M.; Suwa, M.; Kobiro, K.; Kakiuchi, K.; Gleiter, R. *J. Am. Chem. Soc.* **1990**, *112*, 8889.

(14) (a) Günther, H.; Schmitt, P.; Fischer, H.; Tochtermann, W.; Liebe, J.; Wolff, C. *Helv. Chim. Acta* **1985**, *68*, 801. (b) Tobe, Y.; Nakayama, A.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. *J. Org. Chem.* **1987**, *52*, 2639 and references cited therein.