

1,6,7,10-Tetramethylfluoranthene: Synthesis and Structure of a Twisted Polynuclear Aromatic Hydrocarbon.

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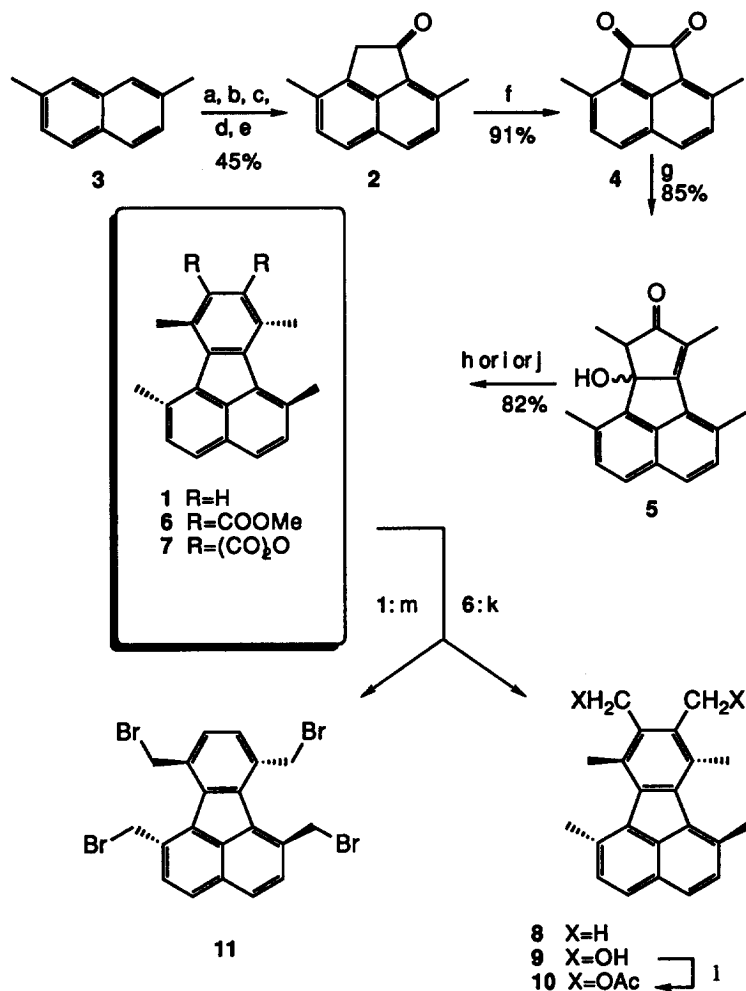
Abstract: The structure and synthesis of the overcrowded polynuclear aromatic 1,6,7,10-tetramethylfluoranthene, **1**, is presented. The structures of **1** and **11** have been determined by X-ray diffraction to be twisted into conformations of approximately C_2 symmetry due to the buttressing of the flanking methyl groups. Semi-empirical calculations (AM1) on **1** find two minima, twist and fold; the twist is of lower energy. The energy for enantiomerization of **1** is set at below 7.0 kcal/mol by variable temperature NMR. Computations predict a likely path to account for the ribbon twist.

Steric crowding in aromatic structures typically results in twisting² or folding³ out-of-plane distortion of the molecule.⁴ Synthesis and elucidation of the stereochemistry of such systems occupies an important position in the chemistry of polynuclear aromatic hydrocarbons.^{5,6} Stereochemical analysis predicts 1,6,7,10-tetramethylfluoranthene (**1**) to be a helically-twisted, strained, aromatic molecule.⁷ This report presents the synthesis and structural characterization of **1** and related compounds.⁸

Modification of an earlier scheme allowed us to prepare 2,7-dimethylacenaphthenequinone⁹ (**4**) from 2,7-dimethylnaphthalene¹⁰ (**3**) in 6 steps (Scheme 1). Condensation of **4** with 3-pentanone and base formed the carbinol **5**. Reaction of **5** with a variety of acetylene equivalents resulted in fluoranthenes **1**, **6**, and **7**. The diester **6** was further derivatized by reduction with lithium aluminum hydride selectively to the diol **9** or exhaustively to 1,6,7,8,9,10-hexamethylfluoranthene (**8**). Treatment of **1** with NBS in carbon tetrachloride yielded **11**.

The X-ray structures of **1**, **6**, and **11** show a helical twist in the aromatic ribbon.^{11,12} The twist is nearly continuous throughout the molecule. The dihedral angle between the best plane through the benzene ring and the best plane through the naphthalene ring is 16° and 18°, respectively, and the dihedral angle between the top bond of the benzene and the vector across the free peri positions in the naphthalene is 19° and 23°, respectively. The proximal C(sp³) to C(sp³) distance in **1** is 3.09 Å and in **11** is 3.25 Å; both fall within the sum of van der Waals (vdW) distance of 4.0 Å. The bromine to bromine distance in **11** is 3.9 Å, close to the sum of vdW radii (Figure 1).

The dynamic stereochemistry of this system in solution was probed through the diacetate **10**. The methylene protons served as a probe of the chirotopicity of the methylene group as a whole. They give rise to an AA' pattern in the fluxional molecule (the achirotopic state), and an AB pattern in the static molecule (the chirotopic state). At -100 °C in deuteriofreon¹³ the methylene protons split out. A dynamic process of ca. 7.0 ± 0.5 kcal/mol was found.¹⁴ On the basis of our previous work on hexasubstituted benzenes,¹⁵ we assigned this



Scheme 1. a) Paraformaldehyde, CH₃CO₂H/HCl, 50 °C, 24 h, 62%; b) KCN, acetone/H₂O, reflux, 12 h, 99%; c) H₂SO₄, CH₃CO₂H, H₂O, reflux, 6 h, 90%; d) SOCl₂, CHCl₃, reflux, 1hr; e) AlCl₃, nitrobenzene, rt, 48 h, 82% (two steps); f) SeO₂, dioxane/H₂O, 60 °C, 48 h; g) 3-pentanone, MeOH, KOH, rt, 30 min; h) Norbornadiene, acetic anhydride, 125 °C, 30 h; i) Maleic anhydride, acetic anhydride; j) Dimethyl acetylenedicarboxylate, acetic anhydride. k) LiAlH₄, THF. l) Acetyl chloride. m) NBS (5 eq.), CCl₄, reflux, 48h.

to the rotation about the C(aromatic)-C(acetoxymethyl) bond and not to the twist interconversion. Nonetheless, this sets an upper limit for the barrier for reversal of the ribbon twist.

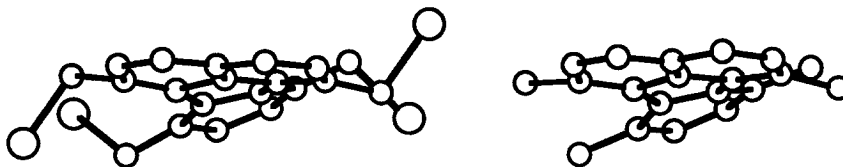


Figure 1. X-ray structures of **1** (right) and **11** (left) showing the twisted (15-20°) aromatic ribbon and juxtaposed methyl groups (3.1-3.3 Å). Picture from MacMoMo, M. Dobler (ETH-Zürich).

Semi-empirical quantum calculations using the AM1 Hamiltonian¹⁶ predict two low energy conformations for **1**, a twist and a fold, with the twist lying ca. 1.2 kcal/mol (2.7 kcal/mol: PCMODEL) below the fold. The geometry of the twist compares favorably with the X-ray data: the twist angle is ca. 15° (**1**, 16°; **11**, 18°: X-ray), and the methyl-to-methyl distance is 3.05 Å (**1**, 3.09 Å; **11**, 3.25 Å: X-ray). The flat conformation lies ca. 15 kcal/mol higher in energy than the twist. From our dynamic NMR work and calculations on similar systems, we can exclude the flat structure as a point on the path to ribbon reversal. The most likely path is twist-fold-twist by way of a transition structure in which only one set of proximal methyl groups pass one another.

Acknowledgements. We thank the National Science Foundation Presidential Young Investigator Award Program (CHE-8857812), and the American Cancer Society Junior Faculty Fellowship Program (C-58024) for support of this work. We greatly appreciate additional support of our program from the Exxon Educational Fund, Hoffmann La Roche, Rohm+Haas, Monsanto, Eli Lilly, Zambon (Italia), and Sterling Drug. We thank the SDSC for a grant of computer time. We thank Dr. Kathleen V. Kilway for help with the variable temperature NMR studies.

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12. a) Crystal Data for **1**: Low temperature data (-100°C) was collected on a crystal ($0.70 \times 0.60 \times 0.20$ mm) grown from benzene/hexane and the structure was solved in $P2_1/c$ ($a = 13.744$, $b = 12.059$, $c = 25.342$, $b = 94.922$; $V = 4184.45 \text{ \AA}^3$; $\rho = 1.23 \text{ g cm}^{-3}$; $Z = 12$). A total of 5468 reflections were collected ($2\theta < 45^\circ$), 3421 were observed ($F_o > 2.0 \text{ s}(F_o)$) to refine anisotropically 541 variable parameters ($R = 7.3\%$, $R_w = 7.2\%$, largest residual 0.35 e/\AA^3). Crystal Data for **11**: Ambient temperature (25°C) data were collected on a crystal ($0.10 \times 0.26 \times 0.45$ mm) grown from hexanes and the structure was solved in P_1 ($a = 10.059$, $b = 10.559$, $c = 10.062$, $a = 92.29$, $b = 118.80$, $g = 92.28$, $V = 934 \text{ \AA}^3$, $\rho = 2.04 \text{ g cm}^{-3}$, $Z = 2$). A total of 5428 reflections were collected ($2\theta < 60^\circ$), 2168 were observed ($F_o > 2.0 \text{ s}(F_o)$) to refine anisotropically 217 variable parameters ($R = 6.6\%$, $R_w = 6.7\%$, largest residual 0.85 e/\AA^3).
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(Received in USA 18 August 1992; accepted 14 October 1992)