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"Fullerene Fragments:" Synthesis and Crystal Structure Determination of 1,4,5,6,7,10,11,12-Octamethylindeno[1,2,3-*cd*]fluoranthene.

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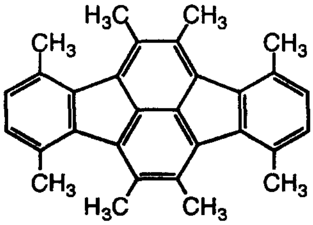
Abstract: The title $C_{30}H_{28}$ hydrocarbon, a potential precursor for the synthesis of buckybowls and carbon cages, is synthesized from 2,3,6,7-tetramethylnaphthalene in eight steps. X-ray crystal structure determination shows a significant distortion of its molecular framework due to steric hindrance of the attached methyl groups. The twisted conformation, present in the solid state, is also predicted to be preferred in the gas phase according to semiempirical AM1 calculations. © 1997 Elsevier Science Ltd.

We have been pursuing the synthesis of polynuclear aromatic hydrocarbons having carbon frameworks that can be identified on the buckminsterfullerene surface. In cases where curvature is a permanent feature of such fullerene fragments, we have referred to these hydrocarbons as buckybowls.[1] As a part of these studies, we became interested in the synthesis of 1,4,5,6,7,10,11,12-octamethylindeno[1,2,3-*cd*]-fluoranthene (**1**) due to the fullerene-like arrangement of its five- and six-membered rings. This $C_{30}H_{28}$ hydrocarbon possesses a carbon network that can be identified on the surface of buckminsterfullerene C_{60} (see illustration), and as such, **1** may be regarded as a potential precursor for large buckybowls and perhaps, carbon cages. Herein we describe a convenient synthesis of this previously unknown hydrocarbon along with its x-ray crystal structure determination that shows a significant nonplanarity of the sp^2 carbon network.



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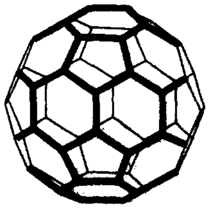
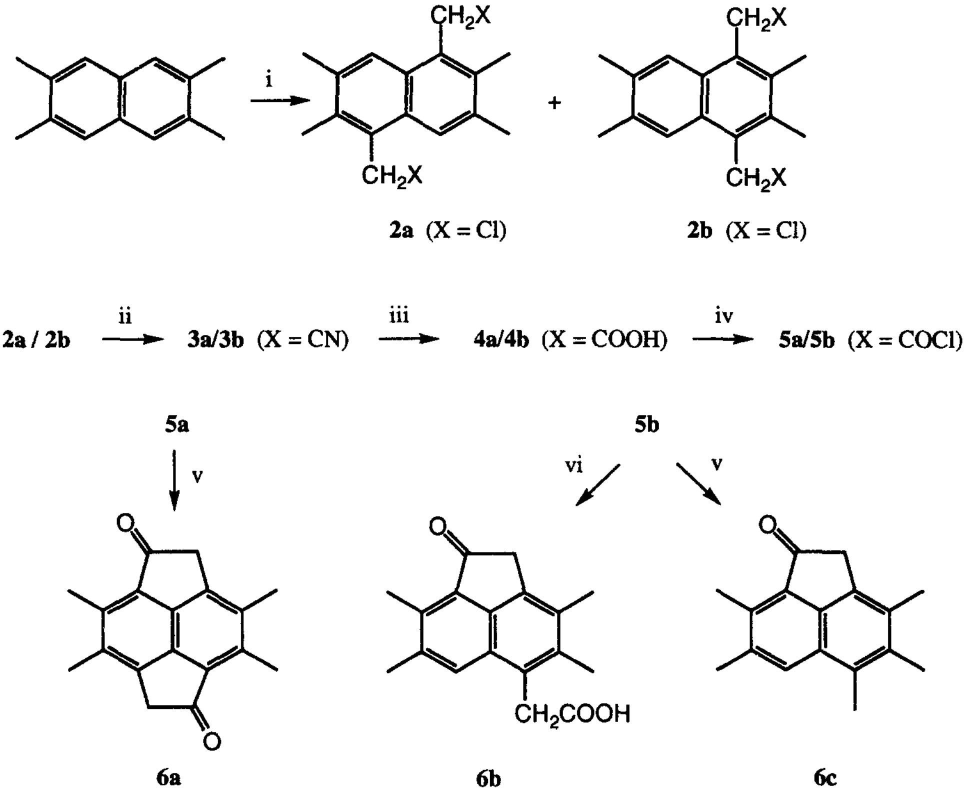


1 on Buckminsterfullerene Surface

The synthesis of **1**, outlined in Schemes 1 and 2,[2] generally followed routes developed by Buu-Hoi and Cagniant,[3] and Siegel, et al.[4] for similar albeit single-sided development of 2,7-dimethylnaphthalene. In the present case, we began with 2,3,6,7-tetramethylnaphthalene[5] which was easily bis-chloromethylated under standard mono-chloromethylation conditions providing a mixture of two isomers **2a** and **2b** in the ratio of approximately 4:1. The isomers were separated by crystallization from toluene, and then quantitatively converted to nitriles **3a** and **3b** by treatment with sodium cyanide in DMSO. Acid catalyzed hydrolysis of the nitriles gave the corresponding acids, **4a** and **4b**, which were subsequently converted to the acid chlorides **5a** and **5b**. An interesting double Friedel-Crafts cyclization of **5a** produced 1,5-diketone **6a** in reasonable yield. This double cyclization is unprecedented in the absence of the four methyl substituents, and activation of the naphthalene moiety by such substitution is clearly substantial. However, we were not able to achieve the analogous double cyclization with **5b** with either CS_2 or nitrobenzene as solvent. The single closure product **6b** was formed in nitrobenzene while higher temperatures in carbon disulfide led to decarboxylation to

Scheme 1

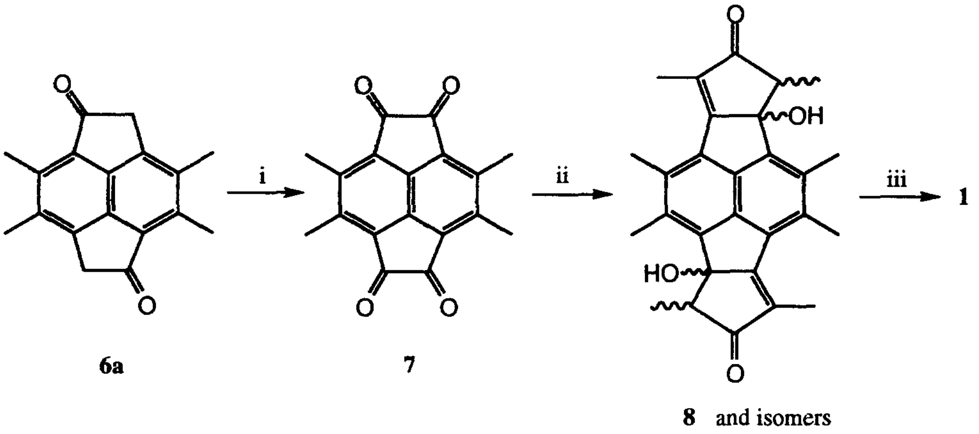


(i) Paraformaldehyde, $HCl/H_3PO_4/CH_3COOH$, 50-60°, 24 hrs; 77%. (ii) NaCN, DMSO, 90°, 3 hrs; quantitative. (iii) $H_2SO_4/H_2O/CH_3COOH$, reflux 12 hrs; 78%. (iv) $SOCl_2$, DCM, reflux 12 hrs. (v) $AlCl_3$, CS_2, r.t., then reflux 12 hrs; 60%. (vi) $AlCl_3$, nitrobenzene, r.t., then 50° for 24 hrs.

produce the pentamethyl monoketone **6c**. It was this difference in chemical behavior between **5a** and **5b** under Friedel-Crafts conditions that led us to make the structural assignments for isomers **2a** and **2b**.

The diketone **6a** was oxidized to tetraketone **7** by selenious acid in dioxane. Tetraketone **7** was then condensed with 3-pentanone in methanol in the presence of potassium hydroxide to produce a mixture of carbinols (**8**); separation of the carbinols was not attempted. Dehydration of **8** followed by Diels-Alder reaction with norbornadiene in acetic anhydride afforded the desired hydrocarbon **1** which was separated from the reaction mixture by column chromatography (silica gel, benzene).[6]

Scheme 2



(i) SeO_2, dioxane/water, reflux 15 hrs; 62%. (ii) 3-pentanone, methanol, KOH, r.t., overnight. (iii) Acetic anhydride/norbornadiene (5:1), reflux 24 hrs; 65% total for steps ii and iii.

Compound **1** crystallizes from benzene/cyclohexane in the form of orange hexagonal plates. Crystal structure determination[7] at 100°K revealed a significant nonplanarity of the sp^2-hybridized carbon network which is clearly a result of the steric hindrance of the four pairs of methyl groups at C1-C12, C4-C5, C6-C7, and C10-C11. The molecule adopts a helical-twisted structure to minimize the repulsion (see Figure 1). Distortion from planarity is indeed significant. The torsional angle between the best planes of the terminal benzene rings is 22°. Even the central naphthalene unit is distorted - the angle between the best planes defined by its two benzene subunits is 6.6°. The carbon atoms of the methyl groups are tilted out of the best planes of the aromatic rings up to 0.4 Å.

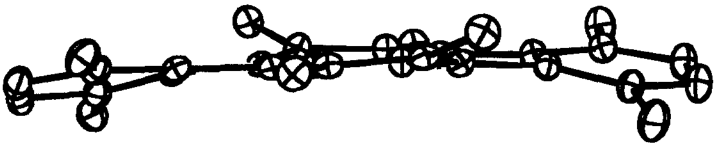
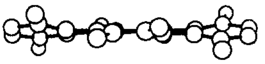
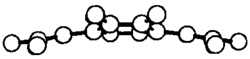


Fig. 1. ORTEP sideview of **1**. Hydrogen atoms omitted for clarity.

The twisted conformation of **1** found in the solid state is also preferred in the gas phase, as predicted by semiempirical AM1 calculations.[8] Of the three distinct minima we located on the potential energy surface of **1** we found the twisted D_2 conformer more stable then both the folded (C_{2v}) and the doubly-folded (C_{2h}) structures by 4.5 and 2.3 kcal/mol, respectively. A similar preference for the twisted vs. folded conformation was previously found for the smaller 1,6,7,10-tetramethylfluoranthene.[4]



twisted, D_2



folded, C_{2v}

doubly-folded, C_{2h}

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2. All intermediate compounds in the synthetic route showed consistent spectral characteristics by ^{1}H and ^{13}C NMR, and by mass spectral analysis.
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6. Orange crystals (from benzene). mp. 268°. ^{1}H NMR (250 MHz; $CDCl_3$) 2.62 (s, 12H), 2.64 (s, 12H), 6.95 (s, 4H). ^{13}C NMR (62.9 MHz; $CDCl_3$) 21.50, 24.46, 130.51, 131.03, 131.48, 133.90, 136.91, 143.07. MS (m/e, rel. intensity) 389(32), 388(100), 373(22), 194(64), 186(23), 179(47), 172(16), 171(30), 170(31), 169(29), 164(30), 163(77), 162(12), 157(41), 150(19).
7. Empirical formula $C_{30}H_{28}$. triclinic, space group P$\bar{1}$, a=7.278(4), b=11.684(2), c=12.589(5) Å, α=101.17(2), β=94.31(4), γ=105.97(3)°, V=1000(1) Å^3, Z=2, D_c=1.290, MoKα radiation, T=100K, R=0.096, Rw=0.065 for 4272 observed data having $1<\theta<32°$ and $I>1\sigma(I)$.
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