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Dimerization of 9-Phenylethynylfluorene to Di-indeno-naphthacene and Dispiro-[fluorene-dihydronaphthacene-fluorene]: An X-ray Crystallographic and NMR Study

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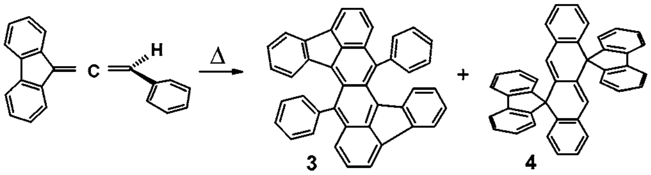
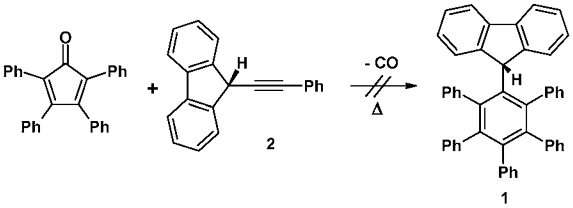
ABSTRACT



The attempted Diels–Alder reaction between 9-phenylethynylfluorene and tetracyclone yields instead three products resulting from the dimerization of the isomeric allene. The major product is 8,16-diphenyl-diindeno[1,2,3-*de*:1′,2′,3′-*mn*]naphthacene, in which each terminal ring is derived from a fluorenyl unit; aerial oxidation then yields a peroxide. A dihydronaphthacene bearing fluorenyl moieties spiro-bonded at the C(5) and C(11) positions was also identified. The structures of the naphthacenes were elucidated by X-ray crystallography, and a mechanistic rationale is offered.

In continuation of our studies on the dynamic behavior of sterically hindered organic or organometallic systems of the general formula C_6Ar_5X, where Ar is phenyl or β-naphthyl and X is phenyl, β-naphthyl, or ferrocenyl,[1] we wished to prepare 9-fluorenylpentaphenylbenzene, **1**. The synthesis required the Diels−Alder addition of 9-phenylethynylfluorene, **2**,[2] to tetraphenylcyclopentadienone (tetracyclone), prior to thermolysis and cheletropic elimination of carbon monoxide (Scheme 1). However, after chromatographic separation to remove unreacted starting materials, three products were isolated and characterized spectroscopically and by

Scheme 1. Attempted Route to Fluorenylpentaphenylbenzene, **1**



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(1) (a) Mailvaganam, B.; Sayer, B. G.; McGlinchey, M. J. *J. Organomet. Chem.* **1990**, *395*, 177. (b) Gupta, H. K.; Brydges, S.; McGlinchey, M. J. *Organometallics* **1999**, *18*, 115. (c) Brydges, S.; Harrington, L. E.; McGlinchey, M. J. *Coord. Chem. Rev.* **2002**, *232−234*, 75. (d) Harrington, L. E.; Britten, J. F.; McGlinchey, M. J. *Can. J. Chem.* **2003**, *81*, 1180.

(2) (a) Dem'yanov, P. I.; Stykow, I. M.; Krut'ko, D. P.; Petrosyan, V. S.; Reutov, O. A. *Metallorg. Khim.* **1988**, *1*, 1039. (b) Dem'yanov, P. I.; Stykow, I. M.; Krut'ko, D. P.; Vener, M. V.; Petrosyan, V. S. *J. Organomet. Chem.* **1992**, *438*, 265. (c) Lee, M. S.; Jackson, J. E. *Res. Chem. Intermed.* **1994**, *20*, 223. (d) Harrington, L. E.; Britten, J. F.; McGlinchey, M. J. *Tetrahedron Lett.* **2003**, *44*, 8057.

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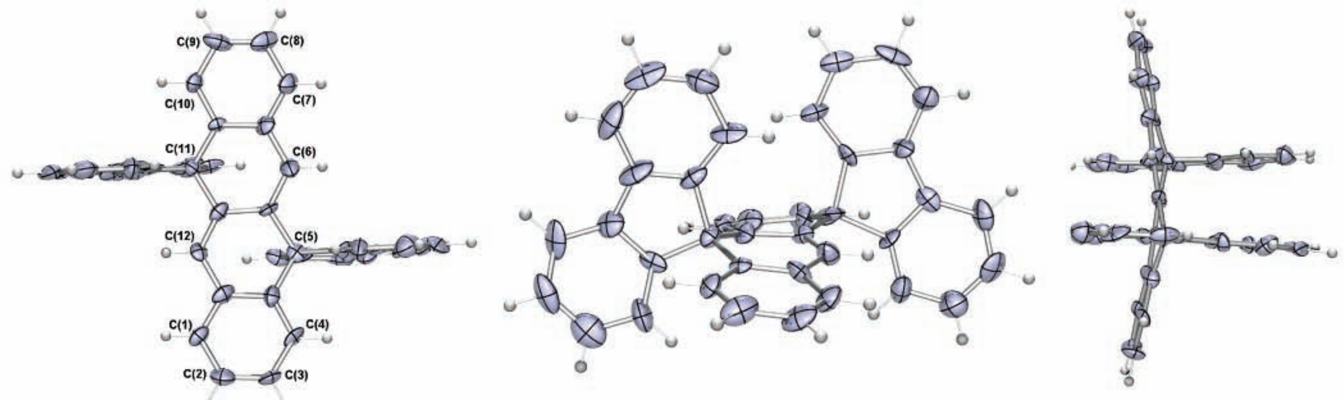


Figure 1. Views of the X-ray crystal structure of dispiro-[fluorene-dihydronaphthacene-fluorene], **4** (30% thermal ellipsoids).

X-ray crystallography, none of which was the desired Diels−Alder adduct. We here describe these three products and offer a mechanistic rationale.

The attempted synthesis of **1** required the use of the relatively harsh conditions necessary to drive Diels−Alder reactions. However, rather than yielding the substituted benzene derivative, **1**, the synthesis led instead to a complex mixture of products that proved to be difficult to separate and identify. The most abundant fraction (45%) was a blue material, **3**, that gave a yellow solution in dichloromethane when exposed to air and light. The identity of this product was not immediately evident, though the fragments present in the molecule could be deduced from the NMR spectrum.

The second major fraction (13%) was a yellow solid, which did not appear to arise from decomposition of the blue product. However, this compound readily formed large crystals that were suitable for an X-ray crystallographic investigation. The X-ray crystal structure revealed the presence of two molecules that had fortuitously cocrystallized together, allowing the identification of both products. The structures of **4** and **5** are shown in Figures 1 and 2, respectively, and reveal in each case a substituted naphthacene framework.

Molecule **4**, $C_{42}H_{26}$, is a dihydronaphthacene in which fluorenyl groups are bonded in a spiro fashion at the C(5) and C(11) positions. Unlike naphthacene (tetracene), pentacene, and hexacene,[3] the linear tetracylic skeleton in **4** is not planar in the solid state but instead folds about the central bond so as to make a bend angle of 22° and exhibits a slight twist of the central rings. Moreover, the two spiro-bonded fluorenyl substituents, which are aligned essentially orthogonally to their attached six-membered rings, are bent slightly in the opposite direction from the dihydronaphthacene framework, thus producing a flattened saddle-type (C_2) structure.

This deformation contrasts with that observed in rubrene (5,6,11,12-tetraphenylnaphthacene) bearing four $(C_5Ph_5)Ru$ cations, which instead twists about the central bond such that the terminal rings are oriented at 67° to each other.[4] However, in solution, the spectroscopic data for **4** are

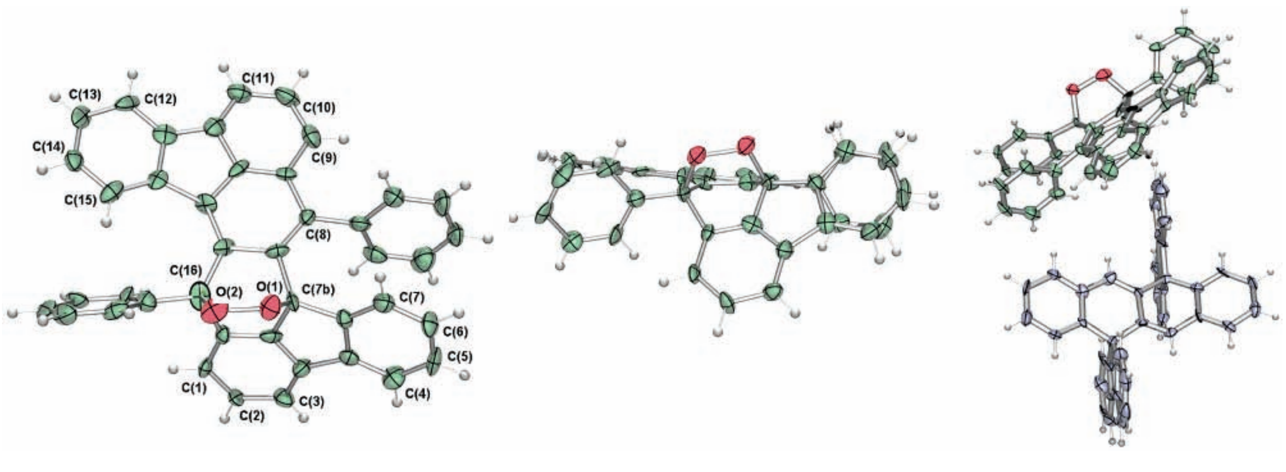
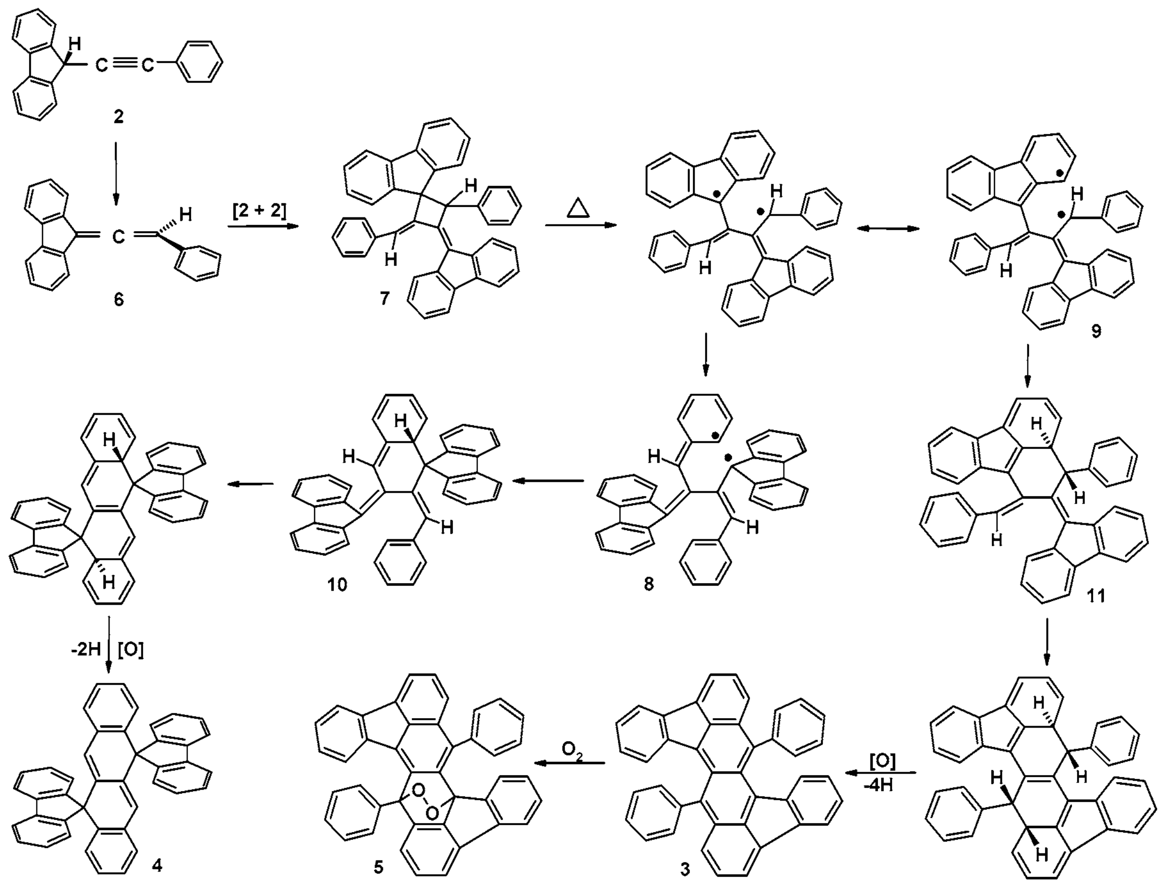


Figure 2. X-ray crystal structure of the di-indeno-naphthacene peroxide **5** (30% thermal ellipsoids) and a plot of the cocrystal, illustrating the relative arrangement of the molecules.

Scheme 2. Proposed Mechanism for the Formation of Products **3**−**5**



consistent with a centrosymmetric molecule of C_{2h} symmetry. The fluorenyl substituents, and also the terminal phenyl rings, each exhibit the expected doublet−triplet−triplet−doublet patterns in the ^{1}H NMR regime.

In **5**, $C_{42}H_{24}O_2$, each terminal ring of the naphthacene skeleton is clearly derived from a fluorenyl moiety, and phenyl substituents are located at C(8) and C(16). Moreover, the C(7b) and C(16) positions are bridged by a peroxy linkage (O−O 1.527(8) Å), thus inducing a folding and twisting of the naphthacene framework such that the dihedral angle between the terminal rings is now 116°. In addition, the phenyl substituent attached at C(8) is stacked parallel to the six-membered ring of the adjacent fluorenyl group. We are unaware of any previous X-ray structures of peroxy-bridged naphthacenes.

In light of these X-ray characterizations, the identity of the blue compound, **3**, was readily established from its ^{1}H NMR spectrum, which exhibited a COSY-connected doublet−triplet−triplet−doublet pattern characteristic of an ortho-disubstituted benzene, a doublet−triplet−doublet sequence for a 1,2,3-trisubstituted benzene, and also a phenyl ring. These data, together with the ^{13}C NMR and mass spectra, are entirely in accord with the assignment of **3** as $C_{42}H_{24}$, the C_{2h}-symmetric naphthacene precursor to the peroxide **5**, as illustrated in Scheme 2. Indeed, when a solution of **3** in dichloromethane was allowed to stand in air and light, the blue color was gradually discharged as oxidation to **5** occurred. A pure sample of **5** was recovered from the decomposition of **3** and identified by high-resolution mass spectrometry and NMR spectroscopy. Compound **5** is not a product of the original reaction but results from decomposition of **3** in solution.

The observed products are evidently not Diels−Alder adducts but rather are derived from the dimerization of 9-phenylethynylfluorene, **2**, presumably via its isomeric allene, **6**, with which it is known to be in equilibrium.[5] The mechanisms of dimerization of allenes have a long and controversial history,[6] but it is now generally understood that initial formation of a bis-alkylidene-cyclobutane is the norm.[7] Thus, when the allene **6** was heated in refluxing heptane, two products were formed:[5] a yellow material (84% yield)

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(3) (a) Campbell, R. B.; Robertson, J. M.; Trotter, J. *Acta Cryst*. **1962**, *15*, 289. (b) Bulgarovskaya, I. V.; Zavodnik, V. E.; Vozzhennikov, V. M. *Acta Crystallogr.* **1987**, *C43*, 764. (c) Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399. (d) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876.

(4) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981.

(5) Kuhn, R.; Rewicki, D. *Chem. Ber.* **1965**, *98*, 2611.

(6) (a) Moureu, C.; Dufraisse, C. *C. R. Acad. Sci. Paris* **1926**, *182*, 1440, 1584. (b) Dufraisse, C.; Etienne, A.; Jolly, J. *C. R. Acad. Sci. Paris* **1950**, *231*, 5. (c) Dufraisse, C.; Mathieu, J.; Valls, J. J. *C. R. Acad. Sci. Paris* **1958**, *246*, 661. (d) Landor, P. D.; Landor, S. R. *J. Chem. Soc*. **1963**, 2707.

(7) Fischer H. In *The Chemistry of Alkenes*; Patai, S., Ed.; Wiley: New York, 1964; Vol. 1, pp 1064−1067.

that was subsequently characterized by X-ray crystallography as the head-to-tail [2 + 2] dimer, **7**,[8] and a red dimer (8%) whose identity remains to be unraveled.

With some prescience, Dreissig, Luger, and Rewicki[8] noted that the bond linking the tetrahedral carbons in the four-membered ring of **7** is very long (1.606 Å) and should therefore cleave readily to yield a 1,4-diradical. Important studies by Capdeveille and Rigaudy,[9] and also by Christl and co-workers,[10] demonstrated the intermediacy of bi-allyl diradicals that can be delocalized onto the ortho positions of neighboring aromatic rings, thus allowing the formation of six-membered rings. In Scheme 2, we show how these ideas can account for the generation of the observed products **3**−**5**.

Cleavage of the initially formed [2 + 2] dimer, **7**, leads to the diradicals **8** and **9** whereby one can envisage coupling either between an *ortho*-phenyl site and the C(9) position of a neighboring fluorenyl ring (to give **10**) or between an *ortho*-fluorenyl position and the benzylic site (leading to **11**). Subsequent disrotatory electrocyclization of the 6π system generates the required molecular frameworks, and aerial oxidation yields the observed products **3** and **4**. It has long been known that linear polyaromatics such as naphthacene or pentacene readily undergo addition of dioxygen,[11] and so, with hindsight, formation and isolation of the peroxide **5** is not unexpected.

We are aware of only one compound closely related to those described here. In the Japanese patent literature, diindeno[1,2,3-*de*:1′,2′,3′-*mn*]naphthacene (i.e., molecule **3** minus the phenyl substituents) is reported to exhibit electroluminescence.[12] Unfortunately, however, its synthesis, color, and other physical properties are not described in the patent. Finally, in light of the present observations, it would be interesting to speculate on the structure of the yet uncharacterized allene dimer derived from 9-(ferrocenylethynyl)fluorene.[13] The organometallic group may stabilize a radical intermediate and so facilitate formation of a naphthacene incorporating ferrocenyl moieties, which may result in interesting redox properties.

To conclude, under Diels−Alder conditions, the allene isomer of 9-phenylethynylfluorene undergoes dimerization reactions to yield 8,16-diphenyl-diindeno[1,2,3-*de*:1′,2′,3′-*mn*]naphthacene (**3**) and dispiro-[fluorene-dihydronaphthacene-fluorene] (**4**). Compound **3** oxidizes in the presence of light and air to give the corresponding peroxide, **5**. X-ray crystal structures of **4** and **5** have been determined, and a mechanistic rationale for their formation has been presented.

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Supporting Information Available: Experimental procedures and characterization for compounds **3**−**5**, as well as X-ray crystallographic collection and refinement details and structural data, with fully labeled thermal ellipsoid plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] Dreissig, W.; Luger, P.; Rewicki, D. *Acta Crystallogr*. **1974**, *B30*, 2037.

[9] (a) Rigaudy, J.; Capdevielle, P. *Tetrahedron* **1977**, *33*, 767. (b) Capdevielle, P.; Rigaudy, J. *Tetrahedron* **1979**, *35*, 2093.

[10] Christl, M.; Rudolph, M.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 2730.

[11] Fieser, L. F.; Fieser, M. *Organic Chemistry*, 3rd ed.; Reinhold: New York, 1956; pp 774−775.

[12] Ikeda, S.; Hosokawa, C.; Arakane, T. Japanese Patent 2001-102173; *Chem. Abstr*. **2001**, *134*, P 287628*e*.

[13] Buchmeiser, M.; Schottenberger, H. *Organometallics* **1993**, *12*, 2472.