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# Toroidal Hopping of a Single Hole through the Circularly-Arrayed Naphthyl Groups in Hexanaphthylbenzene Cation Radical

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Synthesis of a dendritic (soluble) hexanaphthylbenzene derivative is described in which the six naphthyl groups are connected to the central benzene ring in a propeller-shaped arrangement. Observation of multiple oxidation waves in its cyclic voltammogram as well as an intense charge-resonance transition (extending beyond 1600 nm) in its cation radical, generated by laser-flash photolysis using photoexcited chloranil as an oxidant, suggests that a single hole is mobilized via electron transfer (or hopping) over six identical (circularly arrayed) redox centers.

## Introduction

The ready availability of the hexaphenylbenzene (**HPB**) core and the ease with which its vertexes can be decorated with a variety of electro-active functionalities makes it an attractive starting point (or platform) for the construction of dendritic structures with novel light-emitting and charge-transport properties.[1] Our interest in the **HPB** core arises from the fact that it arranges its (six) functionalizable vertexes in a circular array around the central benzene ring in a propeller-shaped structure, and such a cofacial arrangement of the six phenyl groups around the central benzene ring holds promise for a toroidal electronic coupling among the six aryl groups. As such, an electronic coupling in various hexaarylbenzene (**HAB**) derivatives is feasible via an overlap of orbitals on *carbon 1* of the aryls that lie cofacially at a distance of ∼2.9 Å from each other which is much closer than van der Waals contact (∼3.4 Å; see structures below).[2]

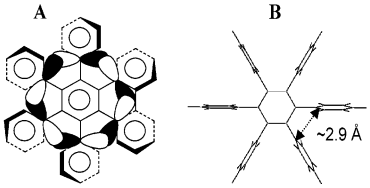

**Figure 1.** Structures showing the orbital overlap among six phenyl groups (A) and the distance between the ipso-carbons of phenyls (B) in hexaphenylbenzene.

For example, we have recently described[3] a versatile synthesis of hexakis(tetraphenylethylene)benzene (**HTB**) in which six tetraphenylethylene moieties are arranged in a circular array around the central benzene ring. Such an arrangement of the tetraphenylethylene moieties allowed a single hole (formed by 1-electron oxidation) to be mobilized via electron transfer (or to hop) over six identical redox-active centers through the hexaphenylbenzene propeller as inferred by the observation of multiple oxidation waves in its cyclic voltammogram as well as the presence of a charge-resonance transition in the near-IR region in its cation radical spectrum. Recently, Kochi and coworkers[4] reported a similar observation of multiple oxidation waves and the presence of a NIR transition in the cation radical spectrum of another hexaarylbenzene derivative, and these observations were reconciled by a similar (toroidal) hole hopping mechanism, as previously suggested by Rathore and coworkers.[3] Our first observation[3] of hole hopping in **HTB** prompted us to explore other structures in this new class of dendritic intervalence materials that may hold promise for the potential applications in the emerging area of molecular electronics and nanotechnology.[5]

Accordingly, herein we will describe the preparation of a hitherto unknown hexanaphthylbenzene derivative in which the six naphthyl groups (instead of phenyls) constitute the propeller of the **HPB** core. The preference of utilizing the naphthyl groups stems from the fact that it possesses rich redox and photochemical properties, which have been extensively investigated using a variety of spectroscopic techniques.[6] Thus, this report describes a facile synthesis of a (soluble) dendritic hexanaphthylbenzene derivative **5** (see Scheme 1) and demonstrate that a single hole in its cation radical is mobilized by hopping over six (identical) naphthyl moieties with the aid of electrochemistry and time-resolved laser-flash photolysis as follows.

## Results and Discussion

As shown in Scheme 1, the synthesis of the dendritic donor **5** was accomplished via a standard five-step route. Thus, 2-bromo-6-hexylnaphthalene (**2**) was obtained by a Friedel−Crafts acylation of 2-bromonaphthalene followed by a reduction using triethylsilane in trifluoroacetic acid. Bromonaphthalene **2** was converted quantitatively to the corresponding iodo derivative **3** by a reaction with magnesium in tetrahydrofuran followed by quenching with iodine at ∼0 °C. The iodonaphthalene derivative **3** was transformed into bis(naphthyl)acetylene **4** in >70% yield using Sonogashira reaction.[7] A trimerization of the resulting acetylene **4** in refluxing dioxane in the presence of a catalytic amount of $Co_2(CO)_8$ afforded the previously unknown hexanaphthylbenzene derivative **5** in >65% yield. The naphthylpentaphenylbenzene **7** was synthesized by a Diels−Alder reaction of phenylnaphthylacetylene **6** with tetraphenylcyclopentadienone in refluxing diphenyl ether. The acetylene **6**, in turn, was obtained by a standard Sonogashira reaction of **3** with phenylacetylene. Another model naphthalene donor **8** was prepared by a Kumada coupling of **2** with 1,3-dimethyl-

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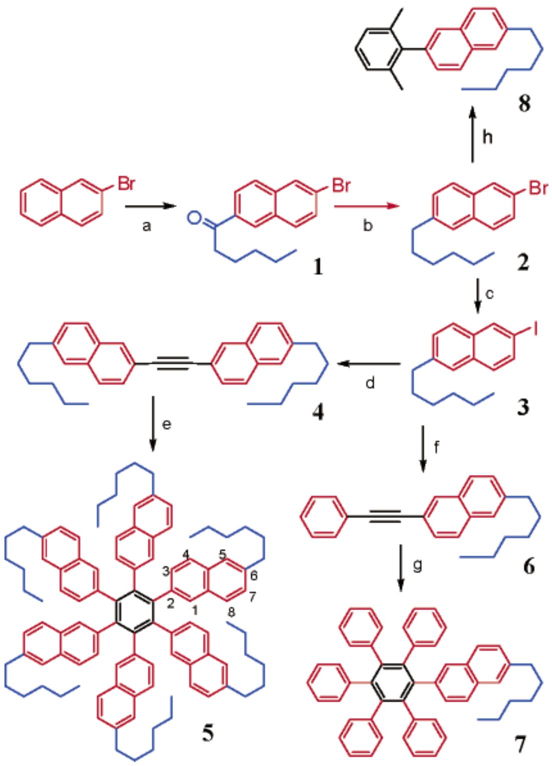
**SCHEME 1: Synthesis of Dendritic Donor 5 and Model Compounds 7 and 8**



[a] Hexanoyl chloride/$AlCl_3$/$PhNO_2$. [b] $Et_3SiH$/$CF_3CO_2H$/$CH_2Cl_2$. [c] Mg, THF/$I_2$. [d] $Me_3Si-CCH$/DBU/benzene/$H_2O$/Pd(II)/CuI. [e] $Co_2(CO)g$/dioxane. [f] Phenylacetylene/CuI/$PPh_3$/$PdCl_2(PPh_3)_2$/triethylamine. [g] $Ph_2O$/tetraphenylcyclopentadienone/reflux. [h] Mg/THF/1,3-dimethyl-2-bromobenzene/$PdCl_2(PPh_3)_2$/reflux.

2-phenylmagnesium bromide in refluxing tetrahydrofuran. The structures of the various molecules in Scheme 1 were established by $^1H/^{13}C$ NMR spectroscopy, mass spectrometry, as well as by correct elemental analysis; see the Experimental Section (Supporting Information) for complete experimental details and the characterization data.

It is well-known that the ortho and meta substituted hexaarylbenzene derivatives exist as mixtures of rotamers due to the restricted rotation around the C−C bonds between the six peripheral aryl groups and the central benzene ring.[8] Indeed, a $^{13}C$ NMR spectrum in Figure 2 revealed the presence of multiple signals in the aromatic region at 22 °C, indicating the presence of multiple rotamers. Moreover, the chemical shifts and the multiplicity of the $^{13}C$ signals remained unchanged upon varying the concentration of **5** (from 7 to 70 mM) and thus confirming that the multiplicity of $^{13}C$ signals does not arise due to the aggregation of **5**. The $^1H/^{13}C$ NMR spectra of **5** in four different solvents (i.e., $CDCl_3$, $CD_2Cl_2$, benzene-$d_6$, and pyridine-$d_5$) showed considerable differences in the chemical shifts of various signals whereas the spectral features remained more or less constant (see Figures S4 and S5 in the Supporting Information). The variable temperature $^1H$ NMR spectra of **5** in $CD_2Cl_2$ (from +20 to −80 °C) did not resolve at lower temperatures; see Figure S6 in the Supporting Information. It should be noted here that the interconversions of various rotamers is not feasible at ambient temperatures due to the high activation barriers.[8]

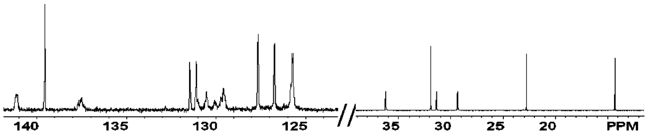


**Figure 2.** $^{13}C$ NMR spectrum of **5** showing multiple peaks for various naphthyl carbons. Note that chemical shifts of the hexyl carbons in the aliphatic region are (relatively) unchanged for various rotamers.

Calculation of the molecular structures of several rotamers of **5** by density functional theory at B3LYP/6-31G* level (using Spartan) showed that the energy difference between various rotamers was <2 kcal $mol^{-1}$. Figure 3 shows the molecular structures of the two representative rotamers in which the naphthyl groups alternate in an up and down orientation (designated as $\mathbf{5}_{135}$) or they all orient in the same direction (designated as $\mathbf{5}_{1-6}$).

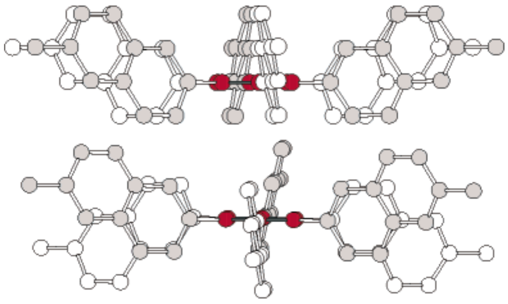


**Figure 3.** Optimized structures (by DFT calculations) of conformers $\mathbf{5}_{1-6}$ (top) and $\mathbf{5}_{135}$ (bottom) of the hexanaphthyl donor **5**.

Consistent with the $^{13}C/^1H$ NMR spectral observations, the rotamers of **5** do not interconvert at ambient temperatures as the rotational barriers for interconversions are expected to be high and similar to those observed for meta-substituted aryl rings in various **HAB** derivatives.[8] Although **5** is obtained as an inseparable mixture of rotamers, the electronic coupling among the six naphthyl groups in various rotamers is expected to be similar because of the structural similarity of the overlapping regions in various rotamers. Note that only the carbon 2 of various naphthyl groups lie at a close van der Waals contact (vide infra).

The UV−vis absorption spectra of parent naphthalene, model naphthyl donors **7** and **8**, and the hexanaphthylbenzene donor **5** were recorded in dichloromethane (see Figure 4) and the spectral data are compared below:

$$\text{naphthalene:} \quad \lambda_{max} = 275 \text{ nm}, \epsilon_{max} = 6000 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\mathbf{5}: \quad \lambda_{max} = 333 \text{ nm}, \epsilon_{max} = 130\,930 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\mathbf{7}: \quad \lambda_{max} = 329 \text{ nm}, \epsilon_{max} = 7200 \text{ M}^{-1} \text{ cm}^{-1}$$

$$\mathbf{8}: \quad \lambda_{max} = 324 \text{ nm}, \epsilon_{max} = 5580 \text{ M}^{-1} \text{ cm}^{-1}$$

Interestingly, the measured molar absorptivity of **5** is found to be drastically higher (i.e., ∼20-fold) than the expected 6-fold increase in comparison to various model compounds. Such an increase in the molar absorptivity of **5** suggests that the circular array of six naphthyl groups forms an extended chromophore because of an effective overlap of the p-orbitals on carbon 2 of the various naphthyl groups.

The electron donor strength of **5** in comparison with its model compounds **7** and **8** were evaluated by electrochemical oxidation at a platinum electrode as a $2 \times 10^{-3}$ M solution in dichloromethane containing 0.2 M $n$-$Bu_4NPF_6$ as the supporting electrolyte. The square-wave voltammogram of **5** showed multiple oxidation waves at a potential of 1.40, 1.57, 1.76 V vs SCE, whereas the model donors **7** and **8**, under identical conditions, showed only one wave each at a potential of 1.56 and 1.66 V, respectively (see Figures S1−S3 in the Supporting

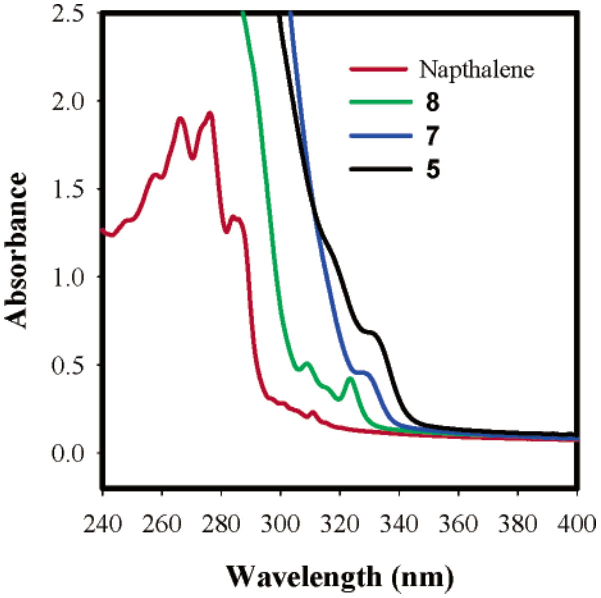


**Figure 4.** UV−vis absorption spectra of parent naphthalene (0.3 mM), hexanaphthylbenzene donor **5** (0.005 mM), and model donors **7** (0.06 mM) and **8** (0.08 mM) in dichloromethane at 22 °C.

Information). The presence of multiple oxidation waves in the voltammograms of **5** (in contrast to the single oxidation wave observed for **7** and **8**) suggests that the removal of first electron from **5** affects the removal of further electrons and thus provides additional indication that the naphthyl moieties arranged in a propeller-shaped structure in **5** are electronically coupled.

As such, the extent of electronic coupling among the circularly arrayed naphthyl moieties in **5** can also be gauged by its significantly lowered oxidation potential, i.e., by 160 mV as compared to the model donor **7** and 260 mV in comparison to the model donor **8**.[9] Moreover, such a through-space electronic coupling between circularly arrayed aryl moieties can also be seen in the electronic spectra of their cation radicals by observation of a highly characteristic charge-resonance transition in the near-infrared region.[3,4] Accordingly, we generated the cation radicals of **5** as well as model donors **7** and **8** based on time-resolved absorption measurements upon diffusional electron-transfer quenching of photoexcited chloranil triplet as an oxidant ($E_{\text{red.}}$ = 2.2 V vs SCE) using laser-flash photolysis as follows.[10]

Thus, the transient spectrum obtained 100 ns after laser excitation (10 ns) of chloranil (4 mM) in the presence of **5** (8 mM) in 1:1 dichloromethane−acetonitrile mixture showed an absorption band at $\lambda_{\max}$ = 450 nm, which is characteristic of a chloranil radical anion,[11] together with an absorption band centered at $\lambda_{\max}$ = 700 and an intense (broad) band extending beyond 1600 nm (see Figure 5). It is noted that the cation radical spectrum of **5** remained unchanged even when generated using different concentrations of **5** (i.e., from 2 to 14 mM) in the above laser-flash photolysis experiment (i.e., Figure 5). The cation radical spectra of model donors **7** and **8** showed absorption bands at 670 and 880 nm and 660 and 890 nm, respectively, and are in agreement with the absorption bands observed for various naphthalene cation radicals.[12] Most importantly, it is noteworthy that the cation radicals of **7** and **8** lacked absorption bands in the near-IR region (see Figure 5) where **5** showed an intense absorption band.

Such an observation of an intense NIR (charge-resonance) transition in $5^{+\bullet}$, which is completely absent in the model cation radicals $7^{+\bullet}$ and $8^{+\bullet}$, can be reconciled by the fact that a rapid hopping of a single hole occurs over six identical naphthyl donors ($N_1$−$N_6$) that are arranged in a propeller shaped structure in **5**, as shown pictorially in Figure 6.

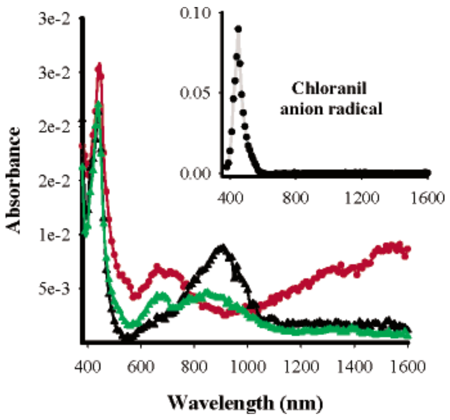


**Figure 5.** Transient absorption spectra of ion radicals from 0.004 M chloranil and 0.008 M **5** (red), **7** (black), and **8** (green) in a 1:3 acetonitrile−dichloromethane mixture following the 10 ns laser excitation at 355 nm. Inset: Absorption spectrum of the chloranil anion radical generated under identical conditions using diaza[2.2.2]bicyclooctane (DABCO) as an electron donor whose cation radical absorbs at <350 nm.

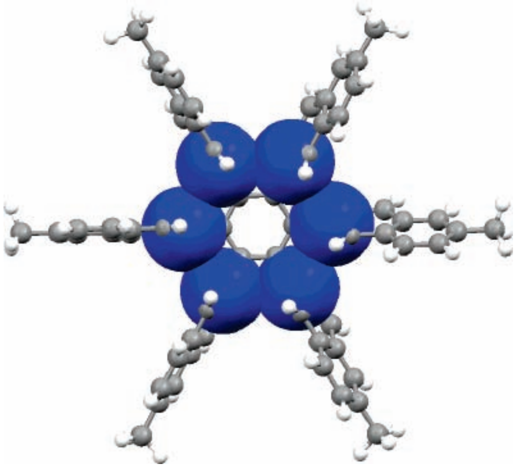


**Figure 6.** Optimized molecular structure of conformer $5_{1-6}$ showing the van der Waals contact between the carbon 2 (blue) of the naphthyl moieties in donor **5**.

**SCHEME 2: Schematic Representation of the Hole Hopping in $5^{+\bullet}$**

The color coding in Scheme 2 essentially describes that a single hole on a naphthyl moiety can hop via electron transfer from one of the two adjacent (naphthyl) donor moieties with equal probability, and occurrence of enough rapid repetitions of this electron-transfer process in $5^{+\bullet}$ ensures that the hole migrates on all naphthyl moieties. We believe that the rate of hole hopping among various naphthyl moieties in $5^{+\bullet}$ should occur on a time scale similar to that in dimeric cation radicals.[13]

The hopping of a single hole over six naphthyl moieties (**N**) in $5^{+\bullet}$ is based on the fact that a cofacial orientation of the phenylene moieties even at 120° in various ethanoanthracene derivatives allows extensive electronic coupling, as established by the observation of intense charge-resonance bands in the NIR region.[13,14] It is also important to emphasize that the hole in

$\mathbf{5}^{+\bullet}$ cannot hop on various naphthalene moieties via the central benzene ring as they lie almost perpendicular to the central benzene ring.[15] Moreover, a limited decrease in the redox potential of **5** in comparison to the model donors **7** and **8** is understandable based on the fact that only carbon 2 of various naphthyl groups participate in the orbital overlap amongst the six redox-acitve groups in **5** and the rest of the carbons on the naphthyl moieties lie at a distance much larger than the sum of the van der Waals contact (see Figure 6).[17] It is also important to emphasize that the hole mobilization in $\mathbf{5}^{+\bullet}$ holds similarity to the observed stabilization of the hexaiodobenzene dication.[16]

In summary, we have synthesized a previously unknown dendritic hexanaphthylbenzene derivative in which the observation of multiple oxidation waves and an intense charge-resonance transition (extending beyond 1600 nm) in its cation radical provides evidence that a single hole is mobilized via electron transfer over six identical redox-active centers that are arranged cofacially in a circular array with a minimal overlap of the naphthyl moieties.[17] Such an observation, coupled with ready preparation of these structures will allow exploration of this new class of intervalence materials in which a hole can hop over multiple (circularly arrayed) redox centers for potential applications for the preparation of photonic devices in the emerging area of molecular electronics and nanotechnology.[1] We are currently engaged in the preparation of novel hexaarylbenzene derivatives that will allow the isolation of stable cation-radical salts for X-ray crystallographic characterization and thereby providing conclusive experimental evidence for the hole delocalization in this new class of dendritic intervalence materials.

**Acknowledgment.** We thank the National Science Foundation (Career Award) for financial support.

**Supporting Information Available:** Cyclic and square-wave voltammograms of **5**, **7**, and **8** and the $^{1}H/^{13}C$ NMR spectra of hexanaphthylbenzene donor **5** at variable temperatures and in different solvents and the synthetic details of various compounds in Scheme 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The difference in lowering of the oxidation potential of **5** in comparison to the model donors **7** (i.e., 160 mV) and **8** (i.e., 260 mV) may be reconciled by the fact that the propeller formed by five phenyls and one naphthyl group in **7** help stabilize a single charge better than **8**, which lacks the propeller structure. Note that such stabilization can be visualized as arising from a weak donor–acceptor interaction amongst adjacent phenyl groups and oxidized naphthyl moiety in **7**.

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