

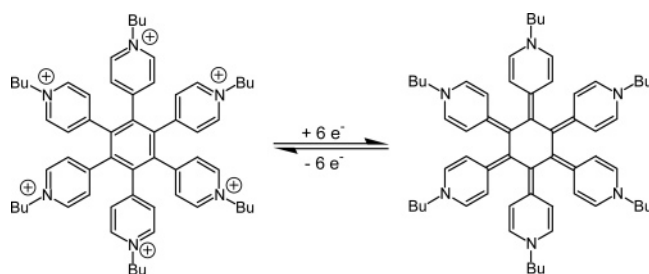
Hexakis(4-(*N*-butylpyridylium))benzene: A Six-Electron Organic Redox System

Zhenfu Han,[‡] Thomas P. Vaid,^{*,‡} and Arnold L. Rheingold[§]

Department of Chemistry and Center for Materials Innovation, Washington University, St. Louis, Missouri 63130, and Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093

vaid@wustl.edu

Received September 4, 2007



The cobalt-catalyzed cyclotrimerization of bis(4-pyridyl)acetylene affords hexakis(4-pyridyl)benzene in moderate yield. Alkylation with *n*-butyltriflate gives hexakis(4-(*N*-butylpyridylium))benzene triflate (**1**⁶⁺), which can be reduced with Na/Hg in DMF to neutral **1**⁰. A single-crystal X-ray diffraction structure reveals that **1**⁰ has a chair-cyclohexane-like core and a [6]radialene structure. Cyclic voltammetry shows that **1**⁶⁺ is reversibly reduced to **1**²⁺ in one four-electron step and **1**²⁺ is reversibly reduced to **1**⁰ in one two-electron step. A reduction by four electrons at one potential is unprecedented for a molecule in which the electrochemically active centers are in electronic communication. The large structural transformation from **1**⁶⁺ to **1**⁰ is responsible for the “potential inversion” in the cyclic voltammetry, and DFT calculations suggest a possible structure for the stable intermediate **1**²⁺. A comparison is made to the electrochemistry and structural transformations in a previously prepared [4]radialene analogue of **1**⁰.

Introduction

Recently, we have synthesized a number of highly reducing, neutrally charged molecules.^{1–5} Those molecules have included the neutral form of phenyl viologen² and the neutral form of an “extended viologen”³ (see Figure 1). A neutral viologen is very easily oxidized to its dication because two quinoid rings become aromatic when two electrons are removed. In our extended viologen in Figure 1, four quinoid rings become aromatic when the neutral molecule is oxidized to the dication. We therefore

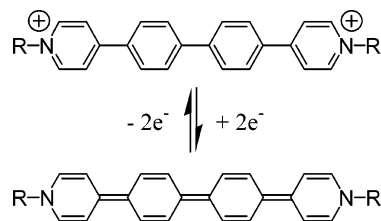


FIGURE 1. The dicationic and neutral forms of an extended viologen.

expected that the neutral extended viologen would be a stronger reducing agent than a regular neutral viologen. Judged by its (2+/0) redox potential, the neutral extended viologen is indeed more reducing than a regular neutral viologen and is in fact the most reducing neutral organic molecule known.³

After our work on the extended viologen, we were interested in investigating the chemistry and electrochemistry of other viologen-like molecules. One intriguing possibility was the hexacation hexakis(4-(*N*-alkylpyridylium))benzene (see Scheme

[‡] Washington University, St. Louis.

[§] University of California, San Diego.

(1) Cissell, J. A.; Vaid, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 12212–12213.

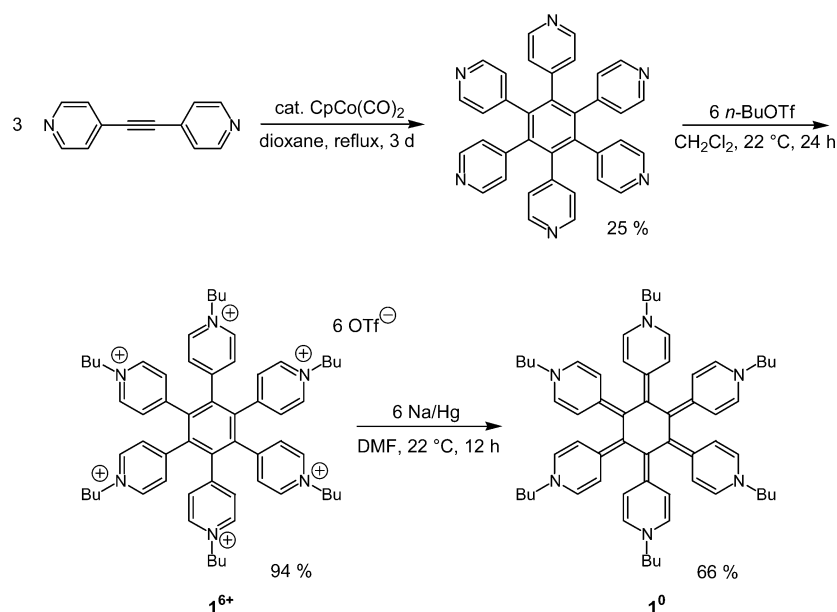
(2) Porter, W. W., III; Vaid, T. P. *J. Org. Chem.* **2005**, *70*, 5028–5035.

(3) Porter, W. W., III; Vaid, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **2005**, *127*, 16559–16566.

(4) Cissell, J. A.; Vaid, T. P.; Rheingold, A. L. *Inorg. Chem.* **2006**, *45*, 2367–2369.

(5) Cissell, J. A.; Vaid, T. P.; Yap, G. P. A. *J. Am. Chem. Soc.* **2007**, *129*, 7841–7847.

SCHEME 1



1 for the structure). It seemed it might be possible to reduce the molecule all the way to its neutral form. The hexacation (with the alkyl group = methyl) had been synthesized previously,^{6,7} but its electrochemistry was not examined, and it seemed that a more straightforward synthetic route might be possible. The cobalt-catalyzed cyclotrimerization of alkynes to benzene derivatives is a thoroughly studied and utilized reaction,⁸ and recently, Müllen and co-workers have made extensive use of the reaction to create hexaarylbenzenes (and then the oxidative cyclodehydrogenation of hexaarylbenzenes to create hexa-*peri*-hexabenzocoronenes).⁹ It seemed that the cobalt-catalyzed trimerization of bis(4-pyridyl)acetylene might provide a convenient route to hexakis(4-pyridyl)benzene, and alkylation would yield the hexacation of interest. Herein we report the synthesis, isolation, and characterization of hexakis(4-(*N*-butylpyridylium))benzene as both a hexacation and neutral molecule.

Results and Discussion

Synthesis. Hexakis(4-pyridyl)benzene and its methylated hexacation hexakis(4-(*N*-methylpyridylium))benzene have been prepared previously.^{6,7} However, that work was focused mainly on the synthesis of tris(pyridylium)propenyl and tris(pyridylium)cyclopropenyl compounds, and it seemed that a more efficient route to hexakis(4-pyridyl)benzene might be possible. We found that the cobalt-catalyzed cyclotrimerization of bis(4-pyridyl)acetylene (available by the bromination and double dehydrobromination of bis(4-pyridyl)ethylene) provides hexakis(4-pyridyl)benzene in 25% yield (Scheme 1). Alkylation of hexakis(4-pyridyl)benzene with *n*-BuOTf in CH₂Cl₂ afforded the hexacation hexakis(4-(*N*-butylpyridylium))benzene triflate (**1⁶⁺** triflate) in 94% yield as a colorless, crystalline solid. Reduction of **1⁶⁺** with sodium amalgam in DMF gave the neutral radialene **1⁰** in 66% yield as a bright yellow, air-sensitive powder.

Crystal Structure of 1⁰. Yellow crystals of **1⁰** were grown by slowly cooling a hot, concentrated solution in toluene to room temperature. The single-crystal X-ray structure of **1⁰** is shown in Figure 2. The C₆ core of **1⁰** has a chair-cyclohexane-like structure, and the bond lengths of **1⁰** (Table 1) match those expected from the pattern of double and single bonds shown for **1⁰** in Scheme 1. The structure of **1⁰** classifies it as a [6]-radialene.^{10,11} Clearly a large structural rearrangement has occurred in the conversion of **1⁶⁺** to **1⁰**, which has implications for the electrochemistry of **1**, as discussed below.

Electrochemistry. The cyclic voltammogram of **1⁶⁺** in DMF is shown in Figure 3. The redox wave at 0 V is due to a ferrocene internal standard. There are two reversible reductions of **1⁶⁺** at -1.14 and -1.33 V (vs Fc^{0/+}). Because **1⁰** was synthesized by the reduction of **1⁶⁺** with Na/Hg in DMF, and the potential of Na/Hg in nonaqueous solvents is about -2.36 V,¹² and no further reductions are observed in the cyclic voltammogram down to -2.50 V, it is very likely that the two observed reduction waves together represent the reduction of **1⁶⁺** to **1⁰**. Because the two redox waves are of unequal magnitude, they cannot be due to two three-electron reductions (**1⁶⁺** → **1³⁺** → **1⁰**) and must be due to either a four-electron and subsequent two-electron reduction (**1⁶⁺** → **1²⁺** → **1⁰**) or a five-electron and subsequent one-electron reduction (**1⁶⁺** → **1¹⁺** → **1⁰**). When the potential is swept at a constant rate (as in this cyclic voltammetry experiment), the peak current, *i_p*, is expected to be proportional to *n*^{3/2}, where *n* is the number of electrons transferred.¹³ For four-electron and two-electron waves, the ratio of the two *i_p* should be 2^{3/2} = 2.83, and for five-electron and one-electron waves, the ratio of the two *i_p* should be 5^{3/2} = 11.2. The experimental ratio of the two *i_p* is 3.16, indicating that it is very likely that the redox processes are **1⁶⁺** + 4 e⁻ ↔ **1²⁺** and **1²⁺** + 2 e⁻ ↔ **1⁰**.

(10) Gholami, M.; Tykwinski, R. R. *Chem. Rev.* **2006**, *106*, 4997–5027.

(11) Hopf, H.; Maas, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 931–954.

(12) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.

(13) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; John Wiley & Sons: New York, 1984.

(6) Breslow, R.; Crispino, G. A. *Tetrahedron Lett.* **1991**, *32*, 601–604.

(7) Crispino, G. A.; Breslow, R. *J. Org. Chem.* **1992**, *57*, 1849–1855.

(8) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860–8871 and references therein.

(9) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718–747.

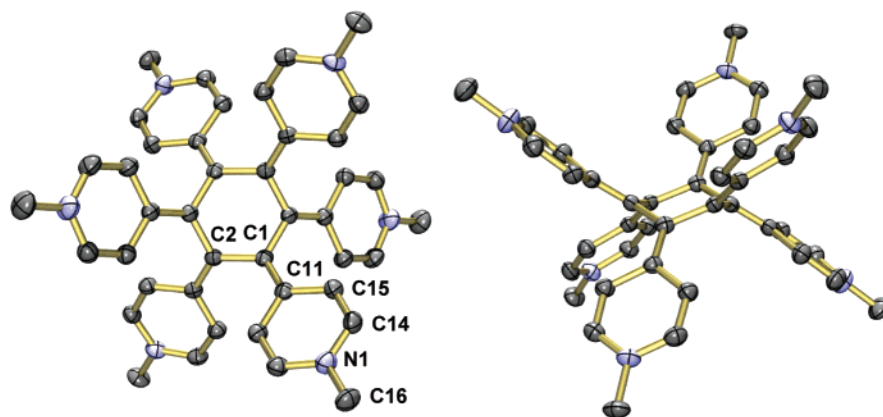


FIGURE 2. Two views of the solid-state structure of the [6]radialene $\mathbf{1}^0$ (only the first carbon of each *n*-butyl group is shown).

TABLE 1. Selected Bond Lengths in the Structure of $\mathbf{1}^0$

bond	length (Å)
C(1)–C(2)	1.489(2)
C(1)–C(11)	1.360(2)
C(11)–C(15)	1.452(2)
C(15)–C(14)	1.336(2)
C(14)–N(1)	1.373(2)
N(1)–C(16)	1.459(2)

Ideally, the separation between the potentials of the peak anodic and peak cathodic currents, ΔE_p , should be 59 mV for the one-electron ferrocene wave, 30 mV for the two-electron $\mathbf{1}^{2+} + 2 e^- \leftrightarrow \mathbf{1}^0$ wave, and 15 mV for the four-electron $\mathbf{1}^{6+} + 4 e^- \leftrightarrow \mathbf{1}^{2+}$ wave.¹³ However, we observe a ΔE_p of 74 mV for ferrocene, 76 mV for the $\mathbf{1}^{2+} + 2 e^- \leftrightarrow \mathbf{1}^0$ wave, and 46 mV for the $\mathbf{1}^{6+} + 4 e^- \leftrightarrow \mathbf{1}^{2+}$ wave (at 50 mV/s sweep rate). The ΔE_p values were similar at sweep rates of 25 and 100 mV/s. These ΔE_p would seem to indicate that the two redox waves observed for $\mathbf{1}$ correspond to two-electron and one-electron processes, but that would mean that $\mathbf{1}^{6+}$ has been reduced only to $\mathbf{1}^{3+}$ in the cyclic voltammetry experiments, and that seems highly unlikely. The reason for the unexpected ΔE_p values is not clear.

Attempts to isolate $\mathbf{1}^{2+}$ by the conproportionation of a 2:1 ratio of $\mathbf{1}^0$ and $\mathbf{1}^{6+}$ were unsuccessful. In polar solvents such as DMF, a 2:1 ratio of $\mathbf{1}^0$ and $\mathbf{1}^{6+}$ yielded dark red solutions, presumably due to the presence of $\mathbf{1}^{2+}$. However, removal of the solvent or addition of a less polar solvent such as ether led to disproportionation of the dark red species to $\mathbf{1}^0$ and $\mathbf{1}^{6+}$. A solution containing $\mathbf{1}^{2+}$ was created by combining $\mathbf{1}^0$ and $\mathbf{1}^{6+}$ in a 2:1 ratio in CH_3CN ; its UV–vis spectrum had absorbances at 232, 259, and 503 nm, with absorptivity ratios of 1.8:1.5:1. The absorbance at 259 nm may be due to $\mathbf{1}^{6+}$.

The $\mathbf{1}^{0/2+}$ potential of -1.33 V shows that $\mathbf{1}^0$ is a moderately strong reducing agent, with an oxidation potential similar to that of cobaltocene.¹² The (0/+) potential of methyl viologen¹⁴ is -1.26 V (vs ferrocene^{0/+}), and the (0/2+) potential of our previously reported four-ring extended viologen (see Figure 1) is -1.48 V.³ The (0/2+) potential of a previously reported three-ring extended viologen¹⁵ is -1.32 V, very similar to that of $\mathbf{1}$.

(14) Baglio, J. A.; Calabrese, G. S.; Harrison, D. J.; Kamieniecki, E.; Ricco, A. J.; Wrighton, M. S.; Zoski, G. D. *J. Am. Chem. Soc.* **1983**, *105*, 2246–2256.

(15) Takahashi, K.; Nihira, T.; Akiyama, K.; Ikegami, Y.; Fukuyo, E. *Chem. Commun.* **1992**, 620–622.

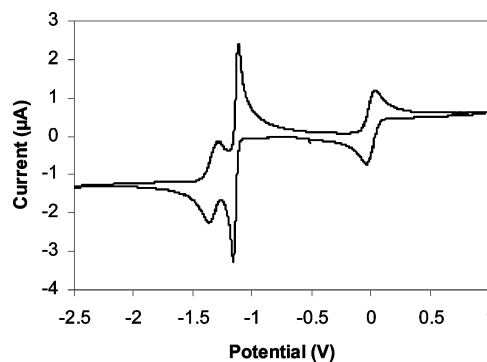


FIGURE 3. Cyclic voltammogram of $\mathbf{1}^{6+}$ in DMF with 0.10 M $[\text{NBu}_4][\text{PF}_6]$, with ferrocene^{0/+} internal standard at 0 V, scan rate 50 mV/s.

Sharp peaks in cyclic voltammograms such as the ones observed for $\mathbf{1}^{6+} + 4 e^- \leftrightarrow \mathbf{1}^{2+}$ are sometimes caused by adsorption of an analyte to the electrode. For a strictly diffusional process, with no adsorption to the electrode, the peak current should be proportional to the square root of the potential sweep rate. We obtained cyclic voltammograms of $\mathbf{1}$ at 25, 50, 100, 150, and 200 mV/s, starting at -0.50 V and sweeping in the negative direction. A plot of the peak reductive current, i_{pc} , for the $\mathbf{1}^{6+} + 4 e^- \rightarrow \mathbf{1}^{2+}$ process versus the square root of the potential sweep rate is linear ($R^2 = 0.997$) with a near-zero intercept (see Figure S1 in Supporting Information). Therefore, it appears that the $\mathbf{1}^{6+} + 4 e^- \leftrightarrow \mathbf{1}^{2+}$ process is diffusion-controlled, and the sharp peaks in the cyclic voltammogram are not due to adsorption.

The reversible oxidation/reduction of a molecule by four electrons at one potential is without precedent, at least for molecules in which the redox-active centers are in electronic communication. There are many examples of molecules with several identical redox-active units that are not in electronic communication and are therefore oxidized or reduced at the same potential. For example, a dendrimer peripherally functionalized with *n* ferrocene units will generally undergo an oxidation by *n* electrons at one potential.^{16–18} In contrast, it is likely that in the reduction of $\mathbf{1}^{6+}$ at least some of the reduction potentials are inverted;¹⁹ in other words, $\mathbf{1}^{5+} + e^- \rightarrow \mathbf{1}^{4+}$ may

(16) Alvarez, J.; Ren, T.; Kaifer, A. E. *Organometallics* **2001**, *20*, 3543–3549.

(17) Sengupta, S. *Tetrahedron Lett.* **2003**, *44*, 7281–7284.

(18) Suzuki, M.; Nakajima, R.; Tsuruta, M.; Higuchi, M.; Einaga, Y.; Yamamoto, K. *Macromolecules* **2006**, *39*, 64–69.

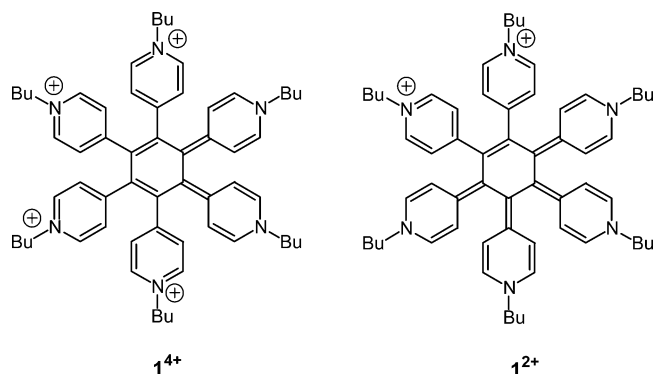


FIGURE 4. Plausible structures for 1^{4+} and 1^{2+} .

have a reduction potential that is more positive than that of $1^{6+} + e^- \rightarrow 1^{5+}$, so both reductions happen at the same potential. That type of potential inversion generally occurs when there is a large structural rearrangement upon electron transfer,¹⁹ and the crystal structure of 1^0 shows that at some point between 1^{6+} and 1^0 a very large structural rearrangement does occur. Density functional theory (DFT) calculations, described below, clarify the structural rearrangements that occur in the reduction steps $1^{6+} \rightarrow 1^{4+} \rightarrow 1^{2+} \rightarrow 1^0$.

DFT Calculations. It has not been possible to isolate **1** in the intermediate oxidation states 1^{2+} or 1^{4+} (or any other intermediate oxidation state), so we undertook DFT calculations on 1^{6+} , 1^{4+} , 1^{2+} , and 1^0 to better understand the intermediate geometries in the large structural rearrangement that occurs in the reduction of 1^{6+} to 1^0 . Simply drawing two valence-bond structures for 1^{4+} and 1^{2+} (Figure 4) suggests one set of plausible structures for 1^{4+} and 1^{2+} . The hexacation 1^{6+} has a benzene-like core, and neutral 1^0 has a chair-cyclohexane-like core, and possible structures for 1^{4+} and 1^{2+} have the 1,3-cyclohexadiene and cyclohexene-like cores, respectively, shown in Figure 4. To convert from the structure of 1^{6+} to the suggested 1,3-cyclohexadiene structure of 1^{4+} , one pair of neighboring peripheral pyridyl rings must twist such that two CH groups move past each other, from “above” the central C_6 ring to “below” the central C_6 ring and vice versa. Similarly, a conversion from the 1,3-cyclohexadiene core to the cyclohexene core requires another set of CH groups to move past each other, as does a conversion from the cyclohexene-like core to the chair-cyclohexane-like core. Those sterically difficult conversions separate the four structures (with benzene, 1,3-cyclohexadiene, cyclohexene, and chair cyclohexane cores) into local energetic minima.

We calculated energy-minimized structures (Gaussian 03,²⁰ B3LYP/6-31G*, with the *n*-butyl groups substituted by methyl groups) for all four oxidation states of concern (1^{6+} , 1^{4+} , 1^{2+} ,

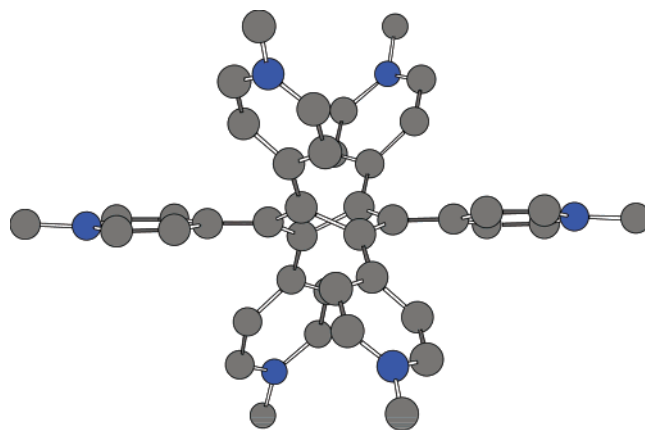


FIGURE 5. View along a C_2 -axis of the calculated (B3LYP/6-31G*) structure of 1^{2+} in the “twisted” geometry, with *n*-butyl groups substituted by methyl groups, and hydrogens not shown.

1^0) starting in all four of the structures outlined above, for 16 total minimizations. For all four oxidation states, the expected geometry (1^{6+} benzene, 1^{4+} 1,3-cyclohexadiene, 1^{2+} cyclohexene, 1^0 chair cyclohexane) was the lowest energy configuration, with the other configurations either higher in energy, or converting to the expected configuration during the minimization, or converting to another geometry altogether that was higher in energy than the global minimum.

In one of the geometry optimizations, when 1^0 was started in the 1,3-cyclohexadiene geometry, the final structure had a C_6 core with a “twisted” geometry. When the structures of 1^{4+} and 1^{2+} were optimized starting from that twisted geometry, they had lower energies than any of the other optimized structures for their respective oxidation states. The optimized structure of 1^{2+} in the twisted geometry is shown in Figure 5. It has overall molecular D_2 symmetry, with three mutually perpendicular C_2 axes. The structure is very similar to that of the dication of hexakis(dimethylamino)benzene, which is discussed further below. It is likely that the twisted D_2 structure is the true global minimum for 1^{2+} , as the calculated energy of the twisted structure is 10 kcal/mol lower in energy than the structure with the next lowest energy, the cyclohexene core structure. The situation is somewhat less clear for 1^{4+} , where the twisted structure has an energy only 2.4 kcal/mol lower than the nearest in energy, the 1,3-cyclohexadiene-like structure. In addition, all the calculations were done without a solvent model, and adding a solvent might change the energy ordering. Neither 1^{2+} nor 1^{4+} has an electric dipole in the twisted structure. In contrast, the cyclohexene-like structure for 1^{2+} has a large calculated dipole moment of 10.4 D, pointing in the direction expected from the valence-bond picture of Figure 4. Similarly, the 1,3-cyclohexadiene structure of 1^{4+} has a calculated dipole moment of 7.1 D, pointing in the direction expected from Figure 4. The presence of a polar solvent may lower the energies of the dipolar structures relative to the twisted structures. However, it is unlikely that a polar solvent would change the relative energetics of the two structures of 1^{2+} by more than 10 kcal/mol, so the twisted structure is likely to be the true global minimum for 1^{2+} . The atomic coordinates for the optimized

(19) Evans, D. H.; Hu, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3983–3990.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.;

Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Wallingford, CT, 2004.

structures of 1^{6+} , 1^{4+} (in both the 1,3-cyclohexadiene and twisted geometries), 1^{2+} (in both the cyclohexene and twisted geometries), and 1^0 are included in the Supporting Information.

Cyclic voltammetry shows that the disproportionation of 1^{4+} to 1^{6+} and 1^{2+} in DMF (eq 1) is thermodynamically favored or has a free energy change very close to zero, while the disproportionation of 1^{2+} to 1^{6+} and 1^0 in DMF (eq 2) has a positive ΔG . The DFT-calculated energies of the relevant species do not shed any light on the energetics of eqs 1 and 2, as they indicate that both disproportionation reactions are disfavored by over 200 kcal/mol. However, the DFT calculations do show that there is one particularly stable structure for 1^{2+} , the twisted structure in Figure 5. The electrochemical behavior of **1** shows that all oxidation states other than 1^0 , 1^{2+} , and 1^{6+} are unstable toward disproportionation. The absence of one particularly favorable structure in the various DFT-optimized geometries of 1^{4+} is at least consistent with that observation.



Comparison to Hexakis(dimethylamino)benzene. The calculated optimal structure of 1^{2+} is similar to that of the dication of hexakis(dimethylamino)benzene. Hexakis(dimethylamino)benzene has the expected planar benzene core, while its dication, which has been characterized crystallographically, has a twisted core like that in Figure 5 and an overall approximate D_2 molecular symmetry.^{21,22} Because of the structural rearrangement, the first two oxidation potentials of hexakis(dimethylamino)benzene are inverted, and it is electrochemically oxidized by two electrons in one step.²² It appears that it is possible to electrochemically oxidize the molecule to the 6+ oxidation state,²³ but no oxidation states higher than 2+ have been isolated.

Another related set of molecules, hexakis(4-(*N,N*-diaryl amino)phenyl)benzenes^{24–27} and hexakis(4-(*N,N*-dialkyl amino)phenyl)benzenes,^{26,28} has been synthesized by cobalt-catalyzed alkyne cyclotrimerization. Those compounds and their (poly)cations were studied electrochemically and spectroscopically. Both the hexakis(4-(*N,N*-diaryl amino)phenyl)benzenes^{24,25} and the hexakis(4-(*N,N*-dialkyl amino)phenyl)benzenes^{26,28} can be oxidized to the 6+ oxidation state, but only the monocations of hexakis(4-(*N,N*-diaryl amino)phenyl)benzenes have been isolated, and none have been structurally characterized.

Comparison to the [4]Radialene Analogue. Two [4]-radialene analogues of 1^0 have been previously synthesized and studied electrochemically; they are pictured as 2^0 in Figure 6, with R = CH₃ or CO₂CH₂CH₃.^{29–31} Cyclic voltammetry showed that 2^0 (R = CO₂CH₂CH₃) can be oxidized in one reversible, two-electron step to the dication 2^{2+} and then in two reversible,

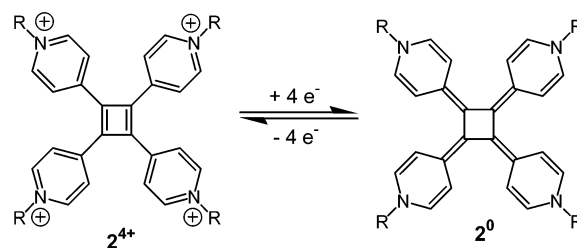


FIGURE 6. The tetracationic and neutral forms of **2** (R = CH₃ or CO₂CH₂CH₃).

one-electron steps to 2^{3+} and 2^{4+} . Similarly, the R = CH₃ version of 2^0 can be reversibly oxidized in a single two-electron step to 2^{2+} , but its oxidation to 2^{3+} is irreversible.

Neither form of **2** (R = CH₃ or CO₂CH₂CH₃) in any of its oxidation states has been structurally characterized. We calculated energy-minimized structures of 2^{4+} , 2^{2+} , and 2^0 (Gaussian 03,²⁰ B3LYP/6-31G*, R = CH₃). The calculated structure of 2^{4+} has the expected cyclobutadiene core and aromatic pyridylum substituents twisted from the plane of the cyclobutadiene core by 38° in a propeller-like arrangement. The neutral 2^0 is a [4]radialene with alternating up and down quinoidal pyridyl groups in a butterfly-like structure. In 2^{2+} , all of the C–C bonds in the cyclobutane core are equivalent and 1.460 Å in length. The pyridyl groups of 2^{2+} are all twisted from the plane of the cyclobutane core by 28° in a propeller arrangement, giving 2^{2+} overall D_4 symmetry. The structural transformations from 2^0 to 2^{2+} to 2^{4+} explain its electrochemical behavior. The structural change from 2^0 to 2^{2+} requires at least one pair of CH groups on neighboring pyridyl groups to twist past each other, a sterically difficult process. There are only two important energetic minima in the structural space of **2**, the propeller-like and butterfly-like geometries, that are separated by a substantial energy barrier. The change between those structures occurs when 2^0 is oxidized to 2^{2+} or 2^{2+} is reduced to 2^0 . The structural rearrangement from 2^{2+} to 2^{4+} has no major energy barrier. Those findings are consistent with the observed inverted potentials for the processes $2^0 - e^- \rightarrow 2^+$ and $2^+ - e^- \rightarrow 2^{2+}$, whereas the potentials for $2^{2+} - e^- \rightarrow 2^{3+}$ and $2^{3+} - e^- \rightarrow 2^{4+}$ are in the normal order (at least for R = CO₂CH₂CH₃, for which those oxidations are observable and reversible).

Conclusions

The reduction of 1^{6+} to 1^0 entails a large structural rearrangement, from the benzene-like core of 1^{6+} to the chair-cyclohexane-like core of the [6]radialene 1^0 . That structural rearrangement explains the potential inversions observed in the cyclic voltammetry of **1**, and DFT calculations suggest a structure for the one stable intermediate oxidation state, 1^{2+} . The four-electron reduction of 1^{6+} to 1^{2+} at one potential is unprecedented for a molecule with electronic communication between the electrochemically active centers.

Experimental Section

Published procedures were employed for the synthesis of bis(4-pyridyl)acetylene³² and butyl triflate.³³

(21) Chance, J. M.; Kahr, B.; Buda, A. B.; Toscano, J. P.; Mislou, K. *J. Org. Chem.* **1988**, *53*, 3226–3232.

(22) Speiser, B.; Würde, M.; Maichle-Mossmer, C. *Chem.—Eur. J.* **1998**, *4*, 222–233.

(23) Speiser, B.; Würde, M.; Quintanilla, M. G. *Electrochem. Commun.* **2000**, *2*, 65–68.

(24) Lambert, C.; Noll, G. *Angew. Chem., Int. Ed.* **1998**, *37*, 2107–2110.

(25) Lambert, C.; Noll, G. *Chem.—Eur. J.* **2002**, *8*, 3467–3477.

(26) Rosokha, S. V.; Neretin, I. S.; Sun, D.; Kochi, J. K. *J. Am. Chem. Soc.* **2006**, *128*, 9394–9407.

(27) Hirao, Y.; Ishizaki, H.; Ito, A.; Kato, T.; Tanaka, K. *Eur. J. Org. Chem.* **2007**, 186–190.

(28) Sun, D.; Rosokha, S. V.; Kochi, J. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 5133–5136.

(29) Horner, M.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 410–411.

(30) Horner, M.; Hünig, S. *Liebigs Ann. Chem.* **1983**, 642–657.

(31) Horner, M.; Hünig, S.; Reissig, H. U. *Liebigs Ann. Chem.* **1983**, 658–667.

Cyclic voltammetry was performed using a potentiostat with electrical connection to the inside of a nitrogen-filled drybox, where all materials and solutions were maintained during the measurements. Cyclic voltammetry was performed in anhydrous DMF with 0.10 M [Bu₄N][PF₆] supporting electrolyte and a ferrocene internal standard. The working electrode and pseudoreference electrode were 0.50 mm diameter platinum disks, and the counter electrode was a 2.5 mm diameter platinum disk.

Hexakis(4-pyridyl)benzene. A solution of bis(4-pyridyl)acetylene (4.680 g, 26.0 mmol) and CpCo(CO)₂ (0.374 g, 2.08 mmol) in 60 mL of dioxane was heated to reflux under N₂ for 3 days. The volatiles were removed by rotary evaporation. The residue was purified by silica gel chromatography with CH₂Cl₂/MeOH (5:1) as the eluent, affording the white product (1.205 g) in 25% yield. The identity and purity of the product were confirmed by comparison of its ¹H NMR spectrum with the reported spectrum.^{6,7}

Hexakis(4-(*N*-butylpyridylium))benzene Triflate (1⁶⁺ Triflate). Butyl triflate (1.591 g, 7.72 mmol) was added to a solution/suspension of hexakis(4-pyridyl)benzene (0.6301 g, 1.17 mmol) in 75 mL of dry CH₂Cl₂, and the mixture was stirred at 22 °C under N₂ for 24 h. The precipitate was collected by filtration and washed with CH₂Cl₂ to furnish hexakis(4-(*N*-butylpyridylium))benzene triflate (1.960 g) in 94% yield as white powder: ¹H NMR (300 Hz, CD₃CN) δ 8.42 (d, *J* = 5.7 Hz, 12H), 8.00 (d, *J* = 5.7 Hz, 12H), 4.31 (t, *J* = 7.5 Hz, 12H), 1.73 (m, 12H), 1.16 (m, 12H), 0.87 (t, *J* = 7.2 Hz, 18H); ¹³C NMR (75 Hz, CD₃CN) δ 154.2, 146.2, 136.8, 131.2, 122.3 (q, *J* = 319 Hz, ⁻O₃SCF₃), 62.7, 33.8, 20.1, 14.0; UV-vis (CH₃CN) 262 nm, log ε = 4.83; IR (Nujol, cm⁻¹) 1642, 1265, 1225, 1158, 1031, 638. Anal. Calcd (found) for C₆₆H₇₈F₁₈N₆O₁₈S₆: C, 44.59 (44.88); H, 4.42 (4.17); N, 4.73 (4.68).

(32) Coe, B. J.; Harries, J. L.; Harris, J. A.; Brunshwig, B. S.; Coles, S. J.; Light, M. E.; Hursthouse, M. B. *Dalton Trans.* **2004**, 2935–2942.

(33) Hong, Y.-R.; Gorman, C. B. *J. Org. Chem.* **2003**, *68*, 9019–9025.

Neutral Radialene (1⁰). Manipulations were carried out on a Schlenk line or in a glovebox under N₂ or vacuum. A solution of hexakis(4-(*N*-butylpyridylium))benzene triflate (1.067 g, 0.600 mmol) in 20 mL of DMF was added to sodium amalgam (Na, 0.0911 g, 3.96 mmol in 10 g Hg). The solution turned violet immediately, then turned dark red after a few minutes. Gradually, the color of the solution became yellow-brown. The mixture was stirred at 22 °C for 12 h. The DMF was removed under vacuum. Benzene (250 mL) was added to the residue, and the suspension was filtered. The volatiles were removed from the filtrate under vacuum to leave a red-brown solid. Ether (30 mL) was added to the residue, forming a red-brown solution with undissolved yellow solid. The solid was collected by filtration and washed with ether to afford the neutral radialene (0.3501 g) in 66% yield as bright yellow powder: ¹H NMR (300 Hz, C₆D₆) δ 5.90 (d, *J* = 8.1 Hz, 12H), 5.78 (d, *J* = 8.1 Hz, 12H), 2.52 (t, *J* = 6.6 Hz, 12H), 1.07 (m, 12H), 0.93 (m, 12H), 0.66 (t, *J* = 7.2 Hz, 18H); ¹³C NMR (75 Hz, C₆D₆) δ 129.8, 121.3, 119.9, 113.0, 53.7, 32.9, 20.1, 14.2; UV-vis (C₆H₆) 321 nm, log ε = 4.83; IR (Nujol, cm⁻¹) 1652, 1407, 1218, 1190, 1048, 1006, 928, 794, 769; HRMS (MALDI) calcd for C₆₀H₇₈N₆ (M⁺) 882.6288, found 882.6285.

Acknowledgment. We thank Prof. Dennis Evans for a helpful discussion, and Dayna Turner for some experimental assistance. Funding was provided by NSF Grant CHE-0133068, and the computational chemistry resource was supported by NSF Grant CHE-0443511.

Supporting Information Available: Crystal structure data in CIF format, crystallographic details, plot of *i*_{pc} vs sweep rate, and coordinate files for the calculated structures of 1⁶⁺, 1⁴⁺, 1²⁺, and 1⁰. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO701944C