

# Electron Transfer Prompted Ejection of a Tightly Bound $K^+$ from the Ethereal Cavity of a Hexaarylbenzene-Based Receptor

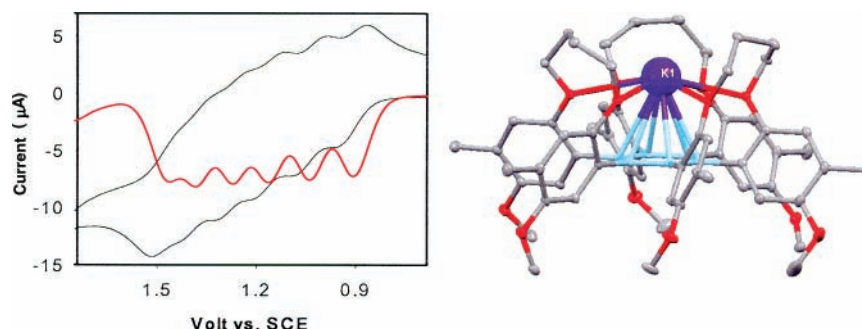
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## ABSTRACT



Synthesis of a pair of rotamers (9u/9s) of a hexaarylbenzene derivative containing six (cofacially arranged) electroactive 2,5-dimethoxytolyl groups is described. The toroidal electronic stabilization due to the circular arrangement of aryl groups in 9u/9s leads to the observation of multiple (reversible) oxidation waves and lowering of their  $E_{ox1}$  by  $\sim 250$  mV relative to model compounds. The binding of  $K^+$  to symmetrical rotamer 9s was monitored by an electrochemical method and further confirmed by X-ray crystallography.

The hexaphenylbenzene (HPB) core has gained considerable attention due to its usage for the preparation of modern graphitic materials<sup>1</sup> that hold potential applications in the emerging areas of molecular electronics and nanotechnology.<sup>2</sup> We<sup>3</sup> and others<sup>4</sup> have recently proposed that the unique propeller-shaped (cofacial) arrangement of the six peripheral aryl groups (such as substituted aniline, naphthalene, and tetraphenylethylene) around the central benzene ring in

various hexaarylbenzene (HAB) derivatives allows a toroidal charge delocalization. To provide unequivocal evidence for the toroidal electronic coupling among the six circularly arrayed aryl groups, we needed to synthesize a HAB derivative that contains the electroactive aryl groups (such as 2,5-dimethoxytolyls)<sup>5</sup> which will undergo reversible electrochemical oxidations at ambient temperature. Unfortunately, attempts to prepare such a HAB derivative (eq 1) by a  $Co_2(CO)_8$ -catalyzed trimerization of bis(2,5-dimethoxytolyl)acetylene (**1**) produced an inseparable mixture of rotamers (**2**) due to the presence of ortho substituents, i.e., eq 1.<sup>6</sup>

(1) (a) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, 101, 1267. (b) Rathore, R.; Burns, C. L. *J. Org. Chem.* **2003**, 68, 4071 and references therein.

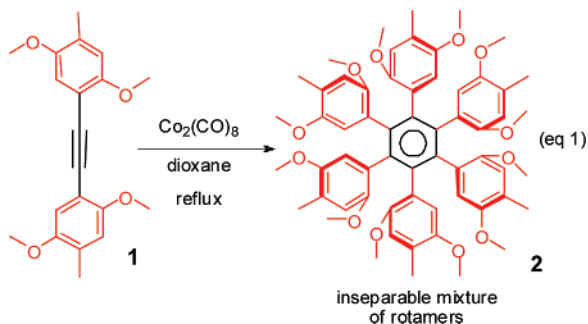
(2) (a) *Introduction to Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Oxford University Press: New York, 1995. (b) Maiya, B. G.; Ramasarma, T. *Curr. Sci.* **2001**, 80, 1523.

(3) (a) Rathore, R.; Burns, C. L.; Abdelwahed, S. H. *Org. Lett.* **2004**, 6, 1689. (b) Chebny, V. J.; Shukla, R.; Rathore, R. *J. Phys. Chem. B* **2006**, 110, 13003.

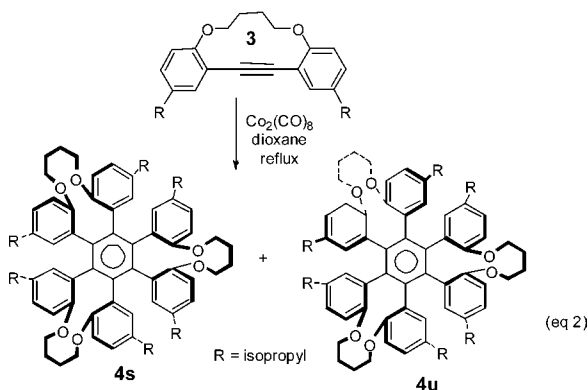
(4) Lambert, C. *Angew. Chem., Int. Ed.* **2005**, 44, 7337 and references therein.

(5) (a) Rathore, R.; Burns, C. L.; Deselnicu, M. I. *Org. Lett.* **2001**, 3, 2887. (b) Chebny, V. J.; Dhar, D.; Lindeman, S. V.; Rathore, R. *Org. Lett.* **2006**, 8, 5401.

(6) Compare: Pepermans, H.; Willem, R.; Gielen, M.; Hoogzand, C. J. *Org. Chem.* **1986**, 51, 301.



We have also recently shown that the problem of formation of the multiple rotamers in eq 1 can be overcome if the trimerization reaction is carried out using a bridged diarylacetylene (such as **3**) which produces only two easily separable rotamers **4u** and **4s**, i.e., eq 2.<sup>7</sup>



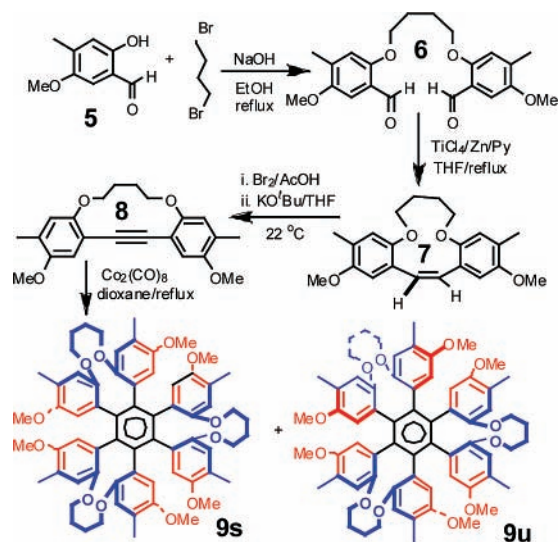
It should also be noted that the symmetrical rotamer **4s** (eq 2), which contains six ethereal oxygens on one face of the central benzene ring, binds a single potassium cation with remarkable efficiency.<sup>7</sup>

It was conjectured that a derivative of **4** which contains electroactive 2,5-dimethoxytolyl groups can be accessed using a procedure similar to eq 2. The availability of these HAB derivatives should allow not only the evaluation of the toroidal electronic coupling but also the monitoring of K<sup>+</sup> binding via an electrochemical method.

Accordingly, we now report the preparation of these HAB derivatives (Scheme 1) which undergo up to six reversible 1-e<sup>-</sup> oxidations that are spanned in the range of ~600 mV. Moreover, the binding of K<sup>+</sup> to the ethereal cavity of the symmetrical rotamer (Scheme 1) is delineated by NMR spectroscopy and X-ray crystallography and can be reversibly controlled by an electrochemical method as follows.

Thus, a reaction of 2 equiv of salicylaldehyde **5** with 1,4-dibromobutane in the presence of NaOH in refluxing ethanol afforded dialdehyde **6** in 95% yield. The McMurry coupling under mild dilution produced a mixture of *cis/trans*-stilbenes **7** in ~85% yield, which were readily converted to the corresponding acetylene **8** by a simple bromination and dehydrobromination reaction sequence<sup>8</sup> in ~80% yield, and

**Scheme 1.** Synthesis of HAB-Based Receptor **9s/9u**



its structure was confirmed by X-ray crystallography (see Supporting Information). A Co<sub>2</sub>(CO)<sub>8</sub>-catalyzed trimerization of **8** in refluxing dioxane for 12 h produced a mixture which upon a chromatographic separation on silica gel (using hexanes and an ethyl acetate mixture as eluent) afforded pure symmetrical isomer **9s** and the unsymmetrical isomer **9u** in ~1:3 ratio in 90% yield, based on the recovered **8** (conversion ~40%). The structures of **9s/9u** were readily established by <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy and were further confirmed by mass spectrometry (see Supporting Information for the experimental details).

Each of the symmetrical and unsymmetrical HAB donors **9s/9u** and a model donor [pentaphenyl(4-methyl-2,5-dimethoxyphenyl)benzene (**10**)] was subjected to electrochemical oxidation at a platinum electrode as a ~2.5 × 10<sup>-4</sup> M solution in a (97:3) dichloromethane–acetonitrile mixture containing 0.2 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. The cyclic and square-wave voltammograms<sup>9a</sup> of **9u/9s** and **10**,<sup>9b</sup> recorded at a scan rate of 100 mV s<sup>-1</sup>, were calibrated with ferrocene as an internal standard and are displayed in Figure 1.

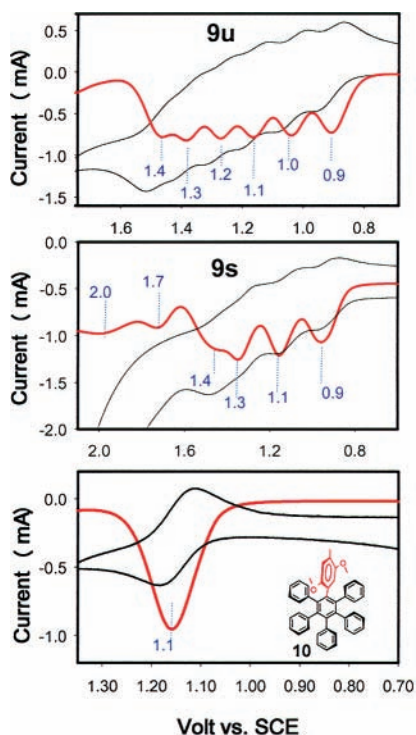
The cyclic voltammogram of **9u** in Figure 1 clearly showed the presence of six well-defined (reversible) oxidation waves at a potential of 0.91, 1.05, 1.17, 1.28, 1.39, and 1.47 V vs SCE, whereas the symmetrical rotamer **9s** showed only four reversible waves at a potential of 0.95, 1.15, 1.34, and 1.45 V (and two irreversible waves at 1.72 and 2.01 V vs SCE).<sup>10</sup> Such an observation of multiple oxidation waves suggests that the removal of the first electron from **9u** (or **9s**) affects the removal of further electrons and thus lends support to the fact that various 2,5-dimethoxytolyl moieties

(7) Shukla, R.; Lindeman, S. V.; Rathore, R. *J. Am. Chem. Soc.* **2006**, *128*, 5328.

(8) Shukla, R.; Lindeman, S. V.; Rathore, R. *J. Org. Chem.* **2006**, *71*, 6124.

(9) (a) Osteryoung, J. G.; Osteryoung, R. A. *Anal. Chem.* **1985**, *57*, 101A. (b) Note that other model compounds such as 2,5-dimethoxy-4,4'-dimethylbiphenyl or hexakis-4'-(4-methyl-2,5-dimethoxybiphenyl)benzene are also oxidized at a potential = 1.16 V vs SCE.<sup>5</sup>

(10) Compare: (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. *J. Am. Chem. Soc.* **1991**, *113*, 7773. (b) Blackstock, S. C.; Selby, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 12155.



**Figure 1.** Cyclic voltammograms of  $2.5 \times 10^{-4}$  M **9u**, **9s**, and **10** (as indicated) in 97:3 dichloromethane–acetonitrile at a scan rate of  $\nu = 100$  mV s $^{-1}$  (22 °C). In each figure, the corresponding square wave voltammograms are also shown in red.

in **9u** (or **9s**) are electronically coupled *due to their propeller-shaped (cofacial) arrangement*.<sup>3,4</sup> As such, the extent of electronic coupling among the circularly arrayed aryl moieties in **9u** (or **9s**) can also be gauged by its significantly lowered oxidation potential, i.e., by 250 mV (or 200 mV) as compared to the model donor **10** ( $E_{\text{ox}} = 1.16$  V vs SCE).<sup>11,12</sup>

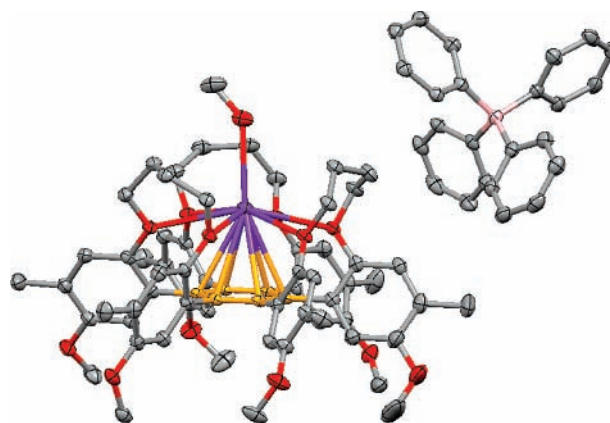
Encouraged by the reversibility of the initial electrochemical oxidations of the symmetrical isomer **9s**, we next examined its binding with the potassium cation as follows. Thus, an exposure of a solution of **9s** in acetone- $d_6$  (0.02 M) to substoichiometric increments of potassium perfluorotetraphenylborate (0.08 M) showed the appearance of a new set of signals in addition to the initial signals due to the uncomplexed **9s** in the  $^1\text{H}$  NMR spectra. As shown in Figure S3 in the Supporting Information, the  $^1\text{H}$  NMR signals due to **9s** were completely replaced by new signals upon addition of 1 equiv of  $\text{K}^+$ . It is noteworthy that the  $^1\text{H}$  NMR spectrum remained unchanged upon further addition of  $\text{K}^+$  solution

(11) (a) It should be noted that the observed lowering of the first oxidation potential in **9u/9s** does not arise due to the mediation of the central benzene ring because of the fact that 1,4-bis(2,5-dimethoxytolyl)durene ejects both of its electrons at a potential of 1.16 V vs SCE. See: Sun, D.; Lindeman, S. V.; Rathore, R.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1585. Also see: (b) Rathore, R.; Abdelwahed, S. H.; Guezzi, I. A. *J. Am. Chem. Soc.* **2003**, 125, 8712. (c) Rathore, R.; Chebny, V. J.; Kopatz, E. J.; Guezzi, I. A. *Angew. Chem., Int. Ed.* **2005**, 44, 2771.

(12) The nature of electronic coupling, i.e., toroidal delocalization vs Coulombic repulsion among the circularly arrayed aryl groups in oxidized **9s/9u**, is presently under investigation.

(i.e., beyond 1 equiv). Moreover, it is noted that the potassium cation is held tightly in the  $[\mathbf{9s}, \text{K}^+]$  complex as it does not undergo a facile exchange with the uncomplexed **9s** on the NMR time scale (at 22 °C). Unfortunately, an accurate binding constant for the formation of  $[\mathbf{9s}, \text{K}^+]$  could not be determined by the NMR method as it simply showed complete capture of  $\text{K}^+$  and suggested that the binding constant is too large to be measured by NMR spectroscopy.<sup>13</sup>

Single crystals of the  $[\mathbf{9s}, \text{K}^+] \text{B}(\text{C}_6\text{H}_5)_4^-$  complex were obtained by a slow evaporation of a  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{OH}$  solution at 22 °C. A molecular structure of the complex with an additional methanol molecule bound to  $\text{K}^+$  was established by X-ray crystallography as shown in Figure 2. The X-ray

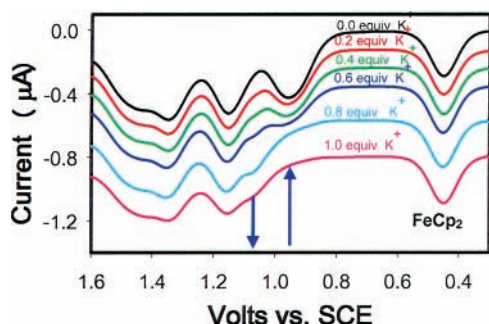


**Figure 2.** ORTEP diagram showing the structure of  $[\mathbf{9s}, \text{K}^+] \text{BPh}_4^-$  with a single  $\text{CH}_3\text{OH}$  molecule complexed to  $\text{K}^+$ . The hydrogens are omitted for clarity.

structure of  $[\mathbf{9s}, \text{K}^+]$  shows that a single potassium cation nestles deep inside the cavity that is comprised of an (hydrophobic) aromatic bottom (i.e., the central benzene ring) with a (hydrophilic) polar etheral fence formed by six oxygens from the peripheral aryl groups. Such a bipolar nature of the cavity in **9s** allows a tight van-der-Waals fit of a single  $\text{K}^+$  cation with a symmetrical  $\eta^6$ -coordination of the  $\text{K}^+$  to the central benzene ring. The distance between the mean plane of the central benzene ring and the  $\text{K}^+$  is 2.808 Å, a distance that is much shorter than the sum of van-der-Waals/ionic radii of carbon and  $\text{K}^+$  (i.e., 3.22 Å). The close  $\text{K}^+ \cdots \text{Ar}$  coordination is a result of the synergy between the cation– $\pi$  interaction and the interaction of the potassium cation with all six etheral oxygens (av  $d_{\text{K}^+ \cdots \text{O}} \sim 2.84$  Å) that are prearranged in a manner analogous to [18]crown-6.

The intimate electronic interactions of the potassium cation with the etheral oxygens from the electronically coupled peripheral aryl groups in  $[\mathbf{9s}, \text{K}^+]$  provided a unique opportunity to monitor the binding of  $\text{K}^+$  using the electrochemical method. Thus, Figure 3 shows the square-wave

(13) Competition experiments indicated that **9s** and [18]crown-6 have a comparable affinity for the potassium cation.



**Figure 3.** Square-wave voltammograms of  $2.5 \times 10^{-4}$  M **9s** in 97:3 dichloromethane–acetonitrile recorded after each addition (as indicated) of substoichiometric increments of  $2.5 \times 10^{-2}$  M  $\text{KB}(\text{C}_6\text{F}_5)_4$  solution in MeCN at 22 °C.

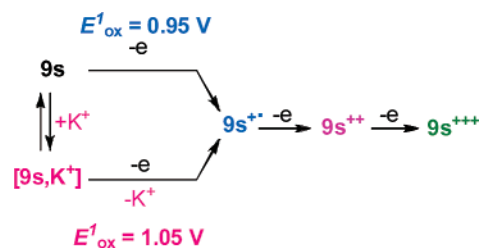
voltammograms obtained by an incremental addition of an acetonitrile solution of  $\text{K}^+ \text{B}(\text{C}_6\text{H}_5)_4$  (25 mM) to a solution of **9s** in a 97:3  $\text{CH}_2\text{Cl}_2$ – $\text{CH}_3\text{CN}$  mixture (0.25 mM), containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte.

Electrochemical titrations of **9s** with  $\text{K}^+$  clearly show that the first oxidation wave (which corresponds to the removal of the first electron) shifts to a higher potential by  $\sim 100$  mV, whereas the other oxidation waves (corresponding to the removal of the second, third, and fourth electron, etc.) remain essentially unchanged. Such an observation can be easily reconciled by the fact that one-electron oxidation of  $[\text{9s}, \text{K}^+]$  to  $[\text{9s}, \text{K}^+]^+$  is accompanied by a concurrent ejection of the  $\text{K}^+$  to avoid Coulombic repulsion among the potassium cation and the ethereal oxygens with partial positive charge (see Scheme 2).<sup>14</sup>

Moreover, the observation of the oxidation waves due to both uncomplexed **9s** and  $[\text{9s}, \text{K}^+]$  in the presence of a substoichiometric potassium cation (see blue arrows in Figure 3) suggests that this redox system or derivative thereof may serve as an electrochemical sensor for the potassium cation.

(14) Note that a positive charge in a *para*-hydroquinone ether stabilizes by a quinoidal distortion where a cationic charge is found largely on the ethereal oxygens. See ref 11a.

**Scheme 2**



In summary, we have accomplished a simple synthesis of hitherto unknown hexaarylbenzene derivatives that contain six (cofacially arranged) electroactive aryl groups. The unsymmetrical isomer **9u** undergoes six (reversible) 1- $e^-$  oxidations which are spanned in the range of  $\sim 600$  mV, thus attesting to the fact that the circularly arrayed aryl groups are electronically coupled.<sup>12</sup> The rotamer **9s** utilizes the symmetrical juxtaposition of the ethereal oxygens to bind a single  $\text{K}^+$  as established by  $^1\text{H}$  NMR spectroscopy and X-ray crystallography. Moreover, the binding of  $\text{K}^+$  to **9s** can be reversibly controlled by electrochemical oxidation, and thus this system meets the necessary criteria for the construction of an electrochemical sensor for the potassium cation.<sup>15</sup> We are currently exploring the potential applications of these materials as well as the isolation of their cation radical salts for the confirmation of toroidal charge delocalization by X-ray crystallography.

**Acknowledgment.** We thank Boulder Scientific Co. for the kind donation of a sample of  $\text{K}^+ \text{B}(\text{C}_6\text{F}_5)_4$ , Ms. M. I. Deselnicu (Marquette University) for preliminary experiments, and the National Science Foundation (CAREER Award) for financial support.

**Supporting Information Available:** Synthetic details,  $^1\text{H}/^{13}\text{C}$  NMR data,  $^1\text{H}$  NMR spectral titration data, and X-ray structural data of **8** and  $[\text{9s}, \text{K}^+]$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) Ross, S. E.; Shi, Y.; Seliskar, C. J.; Heineman, W. R. *Electrochim. Acta* **2003**, *48*, 3313 and references therein.