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Polyaryl Anion Radicals via Alkali Metal Reduction of Arylurea Oligomers

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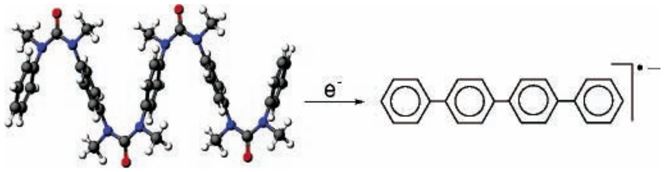
ABSTRACT



A series of *N*-methylated polyarylurea oligomers have been reduced with potassium metal in HMPA. These reductions result in the transient formation of arylurea anion radicals, which undergo reductive elimination of the urea linkages. The aryl moieties appear in the products as the anion radicals of oligoaryl systems. The reaction is intramolecular, and the sequencing in the polyaryl anion radical remains the same as in the polyarylureas due to the urea-enforced π–π stacking interactions.

Due to their use as elements of supramolecular assemblies and devices,[1] semiconductors, and light-emitting diodes, polyphenyls have attracted great interest.[2] The formation of polarons (anion radicals) of these oligomeric materials with alkali metals results in dramatic perturbations in conductivity.[3] Previously, we reported the direct anion radical formation of biaryls from one-electron reductions of biarylureas.[4] In view of the reported promising electronic properties of polyparaphenylene anion radicals and related systems, we were motivated to extend our work to include the formation of polyarene anion radicals. Since polyaryl urea systems can be tailored to include specific aryl groups, in both number and order, we were motivated to develop a technique to directly assemble polyarene polarons with specifically designed sequences of aryl moieties. Such sequencing is analogous to the sequencing of the nucleobases in DNA or RNA.

In our initial efforts to determine the chemical and physical behavior of the first of a series of two-layer tertiary multiarylureas (*N*,*N*′-dimethyl-*N*,*N*′diarylureas), we performed alkali metal reductions in hopes of observing intramolecular delocalization of the anion radical via EPR, as in paracyclophane and paraphenyl systems.[4] We anticipated that these systems might provide through-space delocalized solution analogues of doped biaryl systems. However, the EPR spectra are actually those of the corresponding biaryl anion radicals. We reported that the one-electron reduction of tertiary *N*,*N*′-diarylureas (aryl = phenyl (**I**), 1-naphthyl (**II**), 2-naphthyl (**III**), but not 2-pyrenyl (**IV**), Table 1), in the absence of ion association,[5] results in the formation of the biaryl anion radicals (Table 1 and Scheme 1, $n = 0$).

Continuing our studies of the reductive coupling of diarylureas, we have found that the 2-anthryl system also yields the reduced biaryl. The intramolecular nature of the reductive coupling has been established by the observation of a single product, biphenyl-d_5, upon reduction of the urea **VII** (Table 1) and by the absence of crossover products upon reduction of a mixture of the naphthyl-phenyl urea **VIII** and

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[†] Northwestern University.

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(1) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863. McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.

(2) Braun, D.; Heeger, A. *J. Appl. Phys. Lett.* **1991**, *58*, 1982. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(3) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.

(4) Kurth, T. L.; Lewis, F. D.; Hattan, C. M.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 1460.

(5) Hydrocarbon anion radicals are free from ion association in hexamethylphosphoramide (HMPA); see: Stevenson, G. R.; Echegoyen, L.; Lizardi, L. R. *J. Phys. Chem.* **1972**, *76*, 1439. Shimada, K.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 3321.

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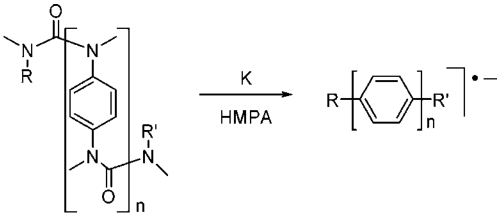
Table 1. Labels Corresponding to Compounds Studied Shown in Scheme 1

parent	*n*	R	R′	product
I	0	phenyl	phenyl	**1**$^{\bullet-}$
II	0	1-naphthyl	1-naphthyl	**2**$^{\bullet-}$
III	0	2-naphthyl	2-naphthyl	**3**$^{\bullet-}$
IV[a]	0	2-pyrenyl	2-pyrenyl	**IV**$^{\bullet-}$
V	0	2-anthryl	2-anthryl	**5**$^{\bullet-}$
VI[a]	0	1-naphthyl	methyl	**VI**$^{\bullet-}$
VII	0	phenyl	phenyl-d_5	**7**$^{\bullet-}$
VIII	0	1-naphthyl	phenyl	**8**$^{\bullet-}$
IX	0	1-naphthyl	phenyl-d_5	**9**$^{\bullet-}$
X	1	phenyl	phenyl	**10**$^{\bullet-}$
XI	2	phenyl	phenyl	**11**$^{\bullet-}$
XII	3	phenyl	phenyl	**12**$^{\bullet-}$
XIII	1	4-biphenyl	4-biphenyl	**12**$^{\bullet-}$
XIV	1	1-naphthyl	1-naphthyl	**14**$^{\bullet-}$

[a] No biaryl formation observed.

the naphthyl-phenyl-d_5 urea **IX**. Reduction of the mononaphthyl urea **VI** yields its anion radical, establishing the requirement of two aryl groups for the occurrence of reductive elimination.

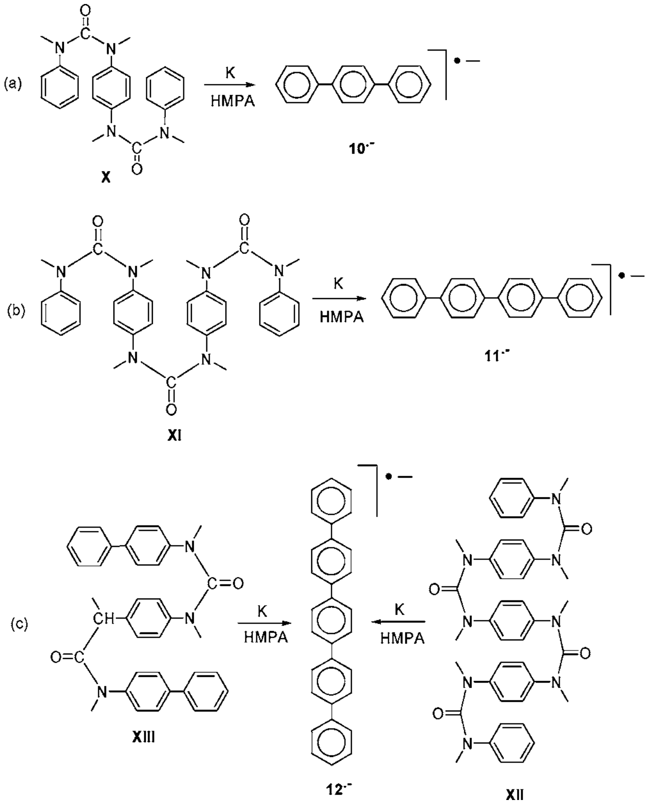
Scheme 1



EPR analysis of the solutions obtained from the reduction of the three- and four-layered polyphenylureas **X** and **XI** with potassium in HMPA solution[5] results in well-resolved EPR signals attributed to the triphenyl and tetraphenyl anion radicals **10**$^{\bullet-}$ and **11**$^{\bullet-}$, respectively (Scheme 2). The EPR spectra of these anion radicals obtained by reduction of the polyphenylenes have been reported by Allred and Bush.[6] Our spectrum for **10**$^{\bullet-}$ can be nicely simulated using their values of a_H. However, the a_H values derived from our spectrum of **11**$^{\bullet-}$ (Figure 1) differ somewhat from those reported.[6]

Further extending the demonstrated ability to form *para*-polyphenyl anion radicals via sequential cleavage of the urea linkages and providing an example of the versatility of this method for production of spectrally observable concentrations of these interesting anion radicals, we synthesized and analogously reduced the tertiary five-layer phenylurea oligomer **XII**. As expected, the anion radical of *para*-pentapheneylene was obtained as **12**$^{\bullet-}$, (Scheme 2c). This spectrum is nearly identical to that reported by Allred and Bush.[6]

Scheme 2



We were, with the aid of the ab initio calculations, able to obtain a good simulation of this spectrum (see Supporting Information). To determine that the formation of polyaryls with mixed aryl groups extends beyond the biaryl systems, the tertiary three-layer biphenyl-phenyl-biphenyl urea **XIII**, Scheme 2, was reduced. The EPR spectrum reveals only a signal for the pentaphenyl anion radical **12**$^{\bullet-}$.

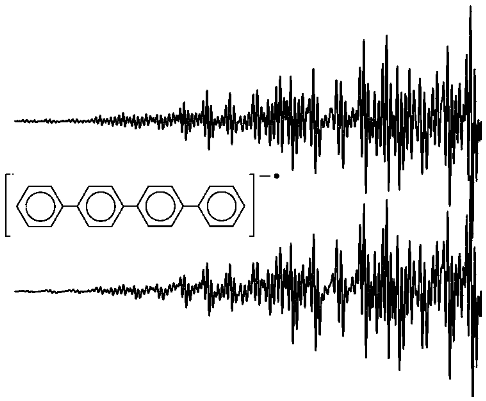


Figure 1. (Upper) Tetraphenyl anion radical **11**$^{\bullet-}$ in HMPA with potassium metal. Low-field half of the EPR spectrum resulting from the potassium reduction of the four-tier polyarylurea shown in Scheme 2. (Lower) Computer simulation using a_Hs of 0.0715, 0.418, 1.336, 1.532 G each for four Hs and an a_H of 1.939 G for a pair of Hs. $\Delta w_{pp} = 0.045$.

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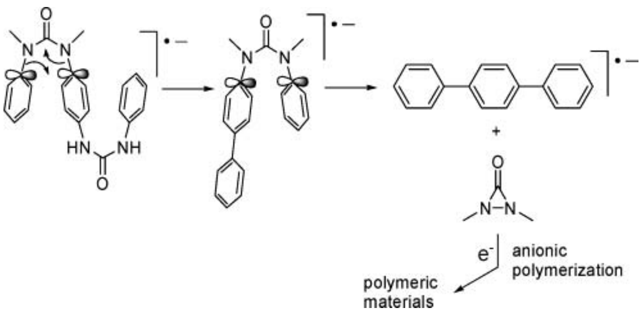
(6) Allred, A. L.; Bush, L. W. *J. Phys. Chem.* **1968**, *72*, 2238.

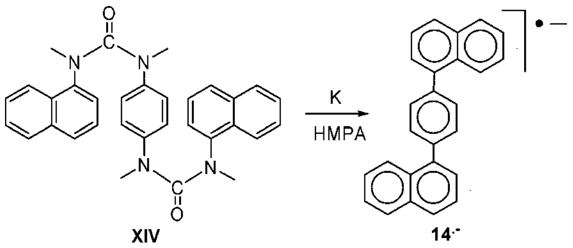
This result is dramatic in that initial reduction of the biphenyl moiety on either end initiates the cleavage of the urea linkage between it and the phenyl moiety. This suggests that the mechanism proposed in our previous report is applicable to polyaryl systems, Scheme 3.[4] One may envision a stepwise cleavage of urea linkages. For example, the intermediate result of the initial urea linkage cleavage of the triphenylurea oligomer **X** is a biphenyl-phenyl urea anion radical (Scheme 3).

Scheme 3



The biphenyl-phenyl-biphenyl result led us to conclude that the oligomeric reaction may be extended to diverse polyaromatic hydrocarbon moieties. As a test, we chose to synthesize and reduce the tertiary three-layer naphthyl-phenyl-naphthyl urea system **XIV**, shown in Scheme 4. As expected, the reduction results in observation of the di-1-naphthyl-paraphenylene anion radical $\mathbf{14}^{\bullet-}$, Figure 2. Reasonable agreement between the B3LYP/6-31G*-predicted spin densities and the empirical spin densities was obtained. There was no delay in the formation of the bis-α-naphthyl-paraphenylene anion radical $\mathbf{14}^{\bullet-}$ after the reduction of the parent urea oligomer. This is in contrast to the delay in formation of the 1-phenylnaphthylene anion radical $\mathbf{8}^{\bullet-}$. It is possible that the naphthyl−phenyl interaction of the unreduced naphthyl moiety lowers the disparity of the ipso carbon position and thus facilitates the initial urea cleavage.

Scheme 4



The ease with which these polyureas "clip together" into their respective polyaryl anion radicals, while preserving sequencing, suggests that some intramolecular inter-arene communication must exist prior to reduction. Indeed, ^{1}H NMR spectra, Figure 3, support this idea. The chemical shifts of the internal phenylenediamine units of **X**−**XIV** display progressive upfield shifts, indicative of the formation of a folded structure in which the phenylene protons are shielded by the neighboring phenyl rings. The influence of the aryl−aryl interaction is demonstrated by the upfield shifts of the central phenyl proton resonances with increasing layers. The influence of naphthyl end-caps on **XIV** is much greater, resulting in a more dramatic shift, Figure 3. The biphenyl end-capped system is not significantly different from the perphenylurea systems.

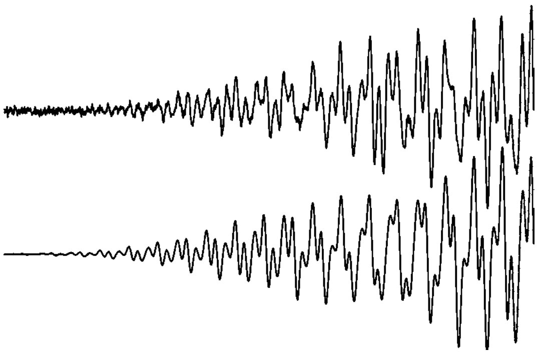


Figure 2. (Upper) Low-field half of the spectrum of $\mathbf{14}^{\bullet-}$ in HMPA, 298 K. (Lower) A computer simulation generated using a_{H}s: 0.6 and 1.63 G for 4 Hs and 1.18, 3.34, 1.60, 0.61, and 0.17 G for proton pairs. $\Delta w_{\mathrm{pp}} = 0.12$ G.

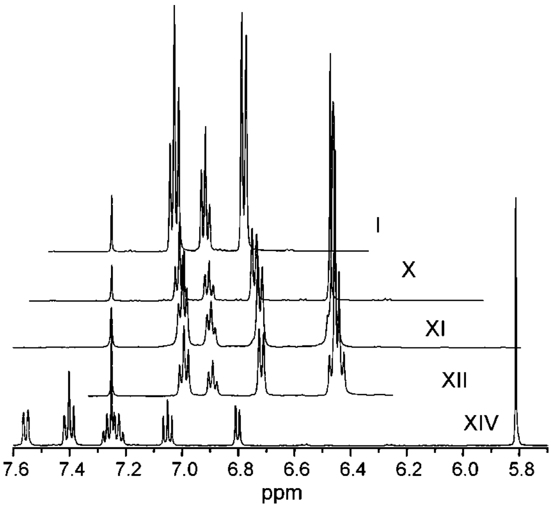


Figure 3. ^{1}H NMR spectra of the arylureas **I**, **X**−**XI**, and **XIV** (500 MHz, $CDCl_3$, 298 K). High-field aromatic protons assigned to the internal phenylenediamines.

The NMR spectral shifts are similar to those recently reported for oligo(dibenzofulvenes), which adopt curved extended structures with π-stacked fluorene rings.[7] These

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[7] Rathore, R.; Abdelwahed, S. H.; Guzel, I. A. *J. Am. Chem. Soc.* **2003**, *125*, 8712.

data are consistent with folded structures in solution, e.g., Figure 4. This DFT/B3LYP-optimized structure strongly resembles that of the crystal structure reported by Shudo et al.[8] The calculated distance between the carbon atoms attached to nitrogen atoms of the urea linkers is ca. 3.0 Å. This is smaller than the sum of the van der Waals radii.

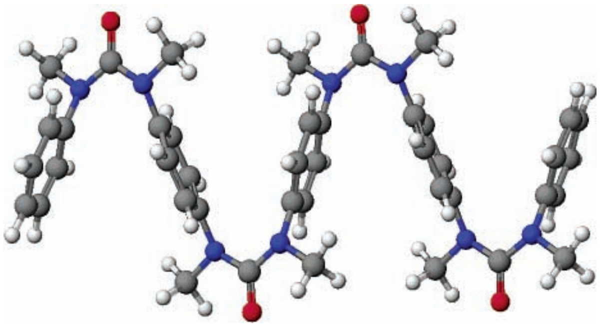

Figure 4. B3LYP/6-31G* (using Spartan 02) minimized structure of the arylurea **XI**.

The sequential appearance of the EPR spectra of **VIII**$^{\bullet -}$ and **8**$^{\bullet -}$ upon reduction of **VIII** indicates that the formation of a naphthalene-localized anion radical precedes loss of the urea linker. The prompt appearance of the biphenyl anion radical **1**$^{\bullet -}$, upon reduction of **I**, and of the 1,1-dinaphthyl anion radical, upon reduction of the corresponding dinaphthylurea, may reflect more effective arene−arene electronic interaction in the symmetric diarylurea anion radicals. Prompt appearance of the polyaryl anion radicals is observed for all of the oligomeric arylureas (**X**−**XIV**). In the absence of EPR spectra for the initially formed arylurea anion radicals, we do not know if these anion radicals are delocalized or localized.

By analogy to the mechanism proposed for the reductive elimination of diarylureas, the elimination of **X**−**XIV** may occur via a sequential nucleophilic addition−elimination mechanism, as shown for urea **X** in Scheme 3. Alternatively, formation of the C−C bond could be followed by a concerted [3 + 2] cycloreversion to yield a biaryl anion radical and *N*,*N*′-dimethyldiaziridinone. Since the product of each elimination step is an anion radical, it is possible that a single electron can effect the elimination of multiple urea linkers. It is fortuitous that the products of interest are observable via EPR, and any diamagnetic products do not obstruct our analysis. The observation of a single component in the EPR spectra suggests that only a single product of low reduction potential is formed.

In summary, the reductive elimination of oligomeric arylureas provides a facile method for directly generating the anion radicals of both polyphenylenes and hybrid naphthalene-phenylene polyaryl systems. In view of the ease of construction of oligomeric aryl ureas from arylamine and diamine building blocks, this method can potentially be used to prepare of a wide variety of doped conducting oligomeric polyaryl systems for EPR characterization. Of special interest will be alternating and block copolymers of arenes, which differ in size (e.g., phenyl and naphthyl) or electron demand (e.g., phenylene and tetrafluorophenylene).

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Supporting Information Available: EPR data obtained from the reduction of **XIII**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[8] DFT/B3LYP-optimized structure strongly resembles that of the crystal structure reported by Shudo et al. Yamaguchi, K.; Matsumura, G.; Kagechika, H.; Azumaya, I.; Ito, Y.; Itai, A.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 5474.