

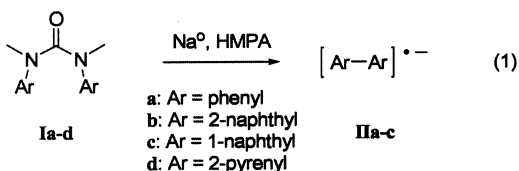
N,N'-Dimethyl-*N,N'*-diarylurea Anion Radicals: An Intramolecular Reductive Elimination

Todd L. Kurth,[†] Frederick D. Lewis,[†] Chris M. Hattan,[‡] Richard C. Reiter,[‡] and Cheryl D. Stevenson*[‡]

Departments of Chemistry, Illinois State University, Normal, Illinois 61790-4160, and Northwestern University, Evanston, Illinois 60208-3113

Received November 1, 2002; E-mail: stevenson@xenon.che.ilstu.edu

Tertiary *N,N'*-diarylureas are unique in their formation of folded structures in which the π systems of the aryl groups interact (Figure 1).¹ Their secondary analogues form extended structures as do diarylpropanes and related molecules. Surprisingly, the physical and chemical properties of the tertiary diarylureas remain relatively unexamined.² In these and similar diaryl systems, π - π interactions are often weak³ but may be augmented by oxidation,⁴ reduction,⁵ intramolecular steric effects, or donor-acceptor substitution.^{1,4} Electronic excitation results in the formation of intramolecular excimers which, in some cases, yield intramolecular adducts.² We were interested in the effects of one-electron reduction of these compounds and the possible existence of fully conjugated anion radicals of these systems. Delocalization of the unpaired electron over both rings presumably would be readily observable via EPR studies. The one-electron reduction of tertiary *N,N'*-diarylureas **Ia-c** (aryl = phenyl, β -naphthyl, α -naphthyl, but not 2-pyrenyl, **Id**) results in the formation of the biaryl anion radicals **IIa-c** (eq 1).



We propose that the diarylurea anion radical (e.g., Figure 1) undergoes a novel intramolecular reductive elimination, wherein the overlapping p_π orbitals on the ipso carbons of opposing aryl groups evolve into a σ bond, forming the biaryl anion radicals.

The reduction of *N,N'*-dimethyl-*N,N'*-diphenylurea (**Ia**) in hexamethylphosphoramide (HMPA), in which ion association does not take place,^{6,7} yields the well-characterized anion radical of biphenyl (**IIa**).⁸ Under identical conditions, *N,N'*-dimethyl-*N,N'*-di- β -naphthylurea (**Ib**) yields a deep blue solution that exhibits an EPR spectrum nearly identical to that previously reported for the β,β' -binaphthyl anion radical (**IIb**).⁹ Analogous reduction of *N,N'*-dimethyl-*N,N'*-di- α -naphthylurea (**Ic**) results in the formation of the α,α' -binaphthyl anion radical (**IIc**). The previously reported EPR analyses have been in disagreement due to solvation effects and misinterpretation of the data.¹⁰ We have generated a precise computer simulation for **IIc** free of ion association (Figure 2).¹¹ The same anion radical also results from the reduction of either *N,N'*-dimethyl-*d*₆-*N,N'*-di- α -naphthylurea or α,α' -binaphthyl. We have reproduced Zingaro's spectrum of **IIc**,¹⁰ in tetrahydrofuran (THF) at 230 K, and corrected the a_{HS} .¹²

Since the possibility existed that biaryl formation occurred from an intermolecular reaction, we carried out the reduction of **Ia** in

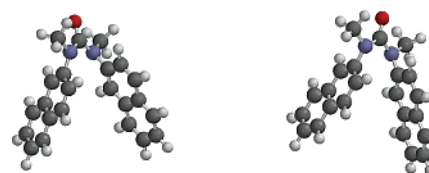


Figure 1. (Left) B3LYP//6-31G* full geometry optimization of **Ib**. (Right) Same for **Ib**^{•-}. The ipso carbons are predicted to be separated by 2.92 Å in **Ib**^{•-} and 3.02 Å in **Ib**.

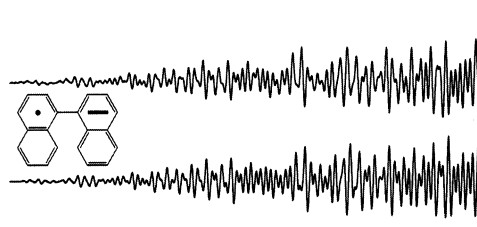


Figure 2. (Upper) Low field half (first 11.18 G) of the X-band EPR spectrum of the anion radical resulting from the reduction of **Ic** with K in HMPA at room temperature. (Lower) A computer simulation generated using a_{HS} of 4.27, 2.295, 1.715, 1.267, 0.908, 0.14, and 0.2 G all for H pairs ($\Delta w_{\text{pp}} = 0.07$ G).

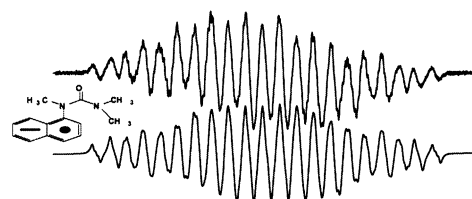


Figure 3. (Upper) X-Band EPR spectrum of the anion radical of *N,N',N'*-trimethyl-*N*- α -naphthylurea resulting from reduction with K in HMPA at room temperature. (Lower) A computer simulation generated using a_{HS} of 1.23, 2.20, 2.40, 4.90, 5.80, 6.10, and 1.32 G, for single Hs, and a 0.20 G splitting from a single ¹⁴N ($\Delta w_{\text{pp}} = 0.22$ G).

the presence of the ring deuterated *N,N'*-dimethyl-*N,N'*-diphenyl-*d*₁₀-urea. This experiment did not result in the formation of any observable biphenyl-*d*₅ (C₆H₅-C₆D₅) anion radical cross-product but rather a simple mixture of the anion radicals of biphenyl and biphenyl-*d*₁₀.⁸ In addition, the one-electron reduction of *N,N',N'*-trimethyl-*N*- α -naphthylurea yields an EPR signal (Figure 3) for the parent anion radical as opposed to the known signal for the α -methylnaphthylene anion radical.¹³ Thus, biaryl formation appears to require the intramolecular reaction of two arenes.

A plausible mechanism for the reductive elimination is outlined in eq 2. The aromatic carbon-nitrogen σ bonds evolve into the p_π orbitals on the ipso carbons of the biphenyl anion radical. Simultaneously, the nonclassically overlapping p_π orbitals evolve into the σ bond joining the phenyl moieties in the anion radical.

[†] Northwestern University.

[‡] Illinois State University.

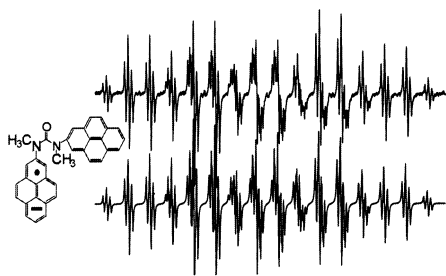
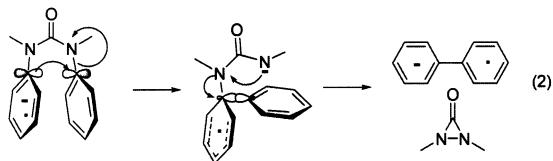


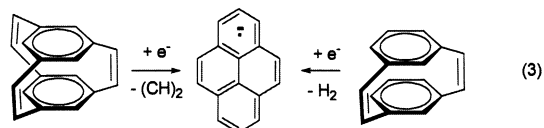
Figure 4. (Upper) X-Band EPR spectrum (13.6 G scan range) of the anion radical of **1d** in HMPA produced by the reduction of the parent compound with potassium metal. (Lower) A computer simulation generated using a_{HS} of 2.527 G (2 Hs), 0.84 G (3 Hs), 0.135 G (2 Hs), 0.031 G (1 H), and 2.44 G (1 N) and a ΔW_{pp} of 0.03 G. The g-tensor anisotropy effects are included.



DFT-optimized structures of the anion radicals (e.g., Figure 1), in accord with the proposed mechanism, indicate that the ipso carbons remain in close proximity. Elimination of N,N' -dimethyldiaziridinone is hypothesized here, as it readily forms in experiments that were expected to lead to the formation of the diradical, such as the photolysis of 1,4-dimethyltetrazolinone.¹⁴ However, the aziridinone is not expected to persist under these very reductive conditions and ultimately leads to polymeric materials.

In contrast to the behavior of **1a–c**, reduction of N,N' -dimethyl- N,N' -di-2-pyrenylurea (**1d**) yields an anion radical that exhibits splittings from a single methyl group and a single ^{14}N (Figure 4). Computer simulation of this EPR spectrum leaves no doubt that the anion radical of **1d** remains intact. In a strict HMO interpretation, the LUMO of pyrene has a nodal plane passing through positions 2 and 7. Hence reduction of **1d** may not result in bonding between the ipso positions. Alternatively, increased charge delocalization and/or aryl–aryl repulsion in the larger anion radical may result in reduced reactivity.

The literature is replete with examples of alkali metal reductions of arenes that lead to biaryl radical anions.^{15,16} Many of these require multielectron reduction or the participation of transition metal cation catalysts. Although proposed mechanisms vary, several have been described as intramolecular in nature, in some cases involving nucleophilic attack of one ring on the other.¹⁷ This is consistent with the mechanism proposed in eq 2. However, the reductive dimerization of tertiary diarylureas is unique in several respects. First, biaryl formation undoubtedly takes place via a one-electron reduction without influence of the metal cation.^{6,18} Second, intramolecular biaryl formation has not been previously observed in a diaryl system linked by a three-atom tether. This exceptional behavior is a direct consequence of the unique orientation of the aryl groups attached to the N,N' -dimethylurea linker. Perhaps the best analogy for the behavior of the diarylureas is provided by alkyl and alkenyl meta arylophanes. Due to the rigidly enforced interaction of the aryl moieties in these systems, their alkali metal reduction leads to formation of a σ bond between the opposing aryl groups and loss of molecular hydrogen and acetylene (e.g., eq 3).¹⁶



Face to face π – π stacking interactions involving aromatic rings are of considerable current interest¹⁹ in part due to their significance in molecular electronics. The biaryl radical anions represents a novel consequence of such interactions. This intramolecular reaction appears to be quite general and not limited to symmetric systems. We have already shown that the N,N' -dimethyl- N -phenyl- N' - α -naphthylurea anion radical quickly eliminates the urea linker to form the anion radical of α -phenylnaphthalene. Since the anion radicals can be readily oxidized to the neutrals, the reductive dimerization of diarylureas offers a method for the synthesis of both symmetric and nonsymmetric biaryls.

Acknowledgment. We thank the National Science Foundation (Grants CHE-9734941, CHE-0100596, and CHE-9617066) for support of this work.

References

- (1) (a) Lepore, G.; Migdal, S.; Blagdon, D. E.; Goodman, M. *J. Org. Chem.* **1973**, *38*, 2590–2594. (b) Tanatani, A.; Kagechika, H.; Azumaya, I.; Fukutomi, R.; Ito, Y.; Yamaguchi, K.; Shudo, K. *Tetrahedron Lett.* **1997**, *38*, 4425–4428.
- (2) Lewis, F. D.; Kurth, T. L.; Liu, W. *Photochem. Photobiol.* **2002**, *1*, 30–37.
- (3) (a) Bushey, M. L.; Hwang, A.; Stephens, P. W.; Nuckolls, C. *J. Am. Chem. Soc.* **2001**, *123*, 8157–8158. (b) Cozzi, F.; Siegel, J. S. *Pure Appl. Chem.* **1995**, *67*, 683.
- (4) Salthi, F.; Lee, B.; Metz, C.; Bottomley, L. A.; Collard, D. M. *Org. Lett.* **2002**, *4*, 3195–3198.
- (5) Baumgarten, M.; Gherghel, L.; Friedrich, J.; Jurczok, M.; Rettig, W. *J. Phys. Chem. A* **2000**, *104*, 1130–1140.
- (6) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Org. Chem.* **1970**, *35*, 1702.
- (7) (a) Stevenson, C. D.; Echegoyen, L.; Lizardi, L. R. *J. Phys. Chem.* **1972**, *76*, 1439–1442. (b) Shimada, K.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 3321–3323.
- (8) EPR spectra of the biphenyl and perdeuterated biphenyl anion radicals and mixtures of the two have been recorded. See: Stevenson, C. D.; Wehrmann, G. C., Jr.; Reiter, R. C. *J. Phys. Chem.* **1991**, *95*, 901–905.
- (9) Konishi, S.; Reddoch, A. H.; Leniart, D. S. *J. Magn. Reson.* **1977**, *28*, 41–51.
- (10) Hnoosh, M. H.; Zingaro, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 4388–4395.
- (11) All EPR spectra were recorded with low modulation amplitude (0.05 G) and a low microwave power to avoid saturation.
- (12) a_{HS} (each for 2Hs) corresponding to the spectrum for α,α' -binaphthyl radical anion in THF at 230 K are 4.36, 2.3, 1.69, 1.27, 0.91, 0.20, and 0.14 G.
- (13) Brumby, S. *J. Magn. Reson.* **1980**, *40*, 157–165.
- (14) (a) Dunkin, I. R.; Shields, C. J.; Quast, H. *Tetrahedron* **1989**, *45*, 259–268. (b) Quast, H.; Bieber, L.; Danen, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1306–1307.
- (15) Biaryl radical anions have been produced via the reduction of tetraphenylmethane, triphenylamine, triphenylboron, triphenylphosphine oxide, phenyl ethers, diphenylsilanes, trinaphthylborane, etc. For references see: (a) Britt, A. D.; Urberg, M. M.; Kaiser, E. T. *J. Org. Chem.* **1966**, *31*, 1661–1662. (b) Wan, Y.-P.; O'Brien, D. H.; Smentowski, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7680–7686. (c) Shine, H. J.; Hughes, L. D.; Gesting, P. *J. Organomet. Chem.* **1970**, *24*, 53–62.
- (16) Gerson, F. *Top. Curr. Chem.* **1983**, *115*, 57–105.
- (17) Leffler, J. E.; Watts, G. B.; Tanigaki, T.; Dolan, E.; Miller, D. S. *J. Am. Chem. Soc.* **1970**, *92*, 6825–6830.
- (18) Cyclic voltammetry reveals only a single irreversible one-electron reduction.
- (19) (a) Miller, G. P.; Mack, J.; Briggs, J. *Org. Lett.* **2000**, *2*, 3983–3986. (b) Prat, F.; Houk, K. N.; Foote, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 845–846. (c) Bjornholm, T.; Greve, D. R.; Reitzel, N.; Hassenkam, T.; Kjaer, K.; Howes, P. B.; Larsen, N. B.; Bogelund, J.; Jayaraman, M.; Ewbank, P. C.; McCullough, R. D. *J. Am. Chem. Soc.* **1998**, *120*, 7643–7644. (d) Nakano, T.; Takewaki, K.; Yade, T.; Okamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9182–9183.

JA0291890