J. Org. Chem. **2001,** *66,* 831−838

Evaluation of the Extent of Conjugation in Symmetrical and Asymmetrical Aryl-Substituted Acetophenone Azines Using Electrochemical Methods

Vittorio A. Sauro and Mark S. Workentin*

Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada

mworkent@julian.uwo.ca

Received August 29, 2000

The electrochemical behavior of a series of symmetrical and unsymmetrical aryl-substituted acetophenone azines (**1**-X/Y, where X and Y are 4-NO_2, 4-CN, H, 3-OCH_3, 4-OCH_3, 4-CH_3, and 4-$N(CH_3)_2$) was studied in acetonitrile and *N*,*N*-dimethylformamide (DMF) solution using cyclic voltammetry (CV). Compounds **1**-X/Y, where neither X or Y are nitro substituents, undergo successive reduction to their radical anion (**1**-X/$Y^{\bullet-}$) and then dianion (**1**-X/Y^{2-}), respectively. In all cases, the formation of the radical anion is completely reversible and the standard reduction potentials, $E^{\circ}_{\mathbf{1}-X/Y/\mathbf{1}-X/Y^{\bullet-}}$ could be determined. The reversibility of the second electron transfer is substituent dependent with certain dianions sufficiently basic to be protonated under our conditions. Standard reduction potentials ($E^{\circ}_{\mathbf{1}-X/Y/\mathbf{1}-X/Y^{\bullet-}}$) for the formation of radical anions exhibit a large substituent effect with values differing by more than 0.66 V throughout the series going from **1**-4-CN/4-CN to **1**-4-OCH_3/4-OCH_3; similar substituent effects were determined for the formation of the dianion. The nitro-containing azines deviate from the above-mentioned behavior. With the exception of **1**-4-NO_2/4-NO_2, they exhibit single electron waves that have values of $E^{\circ}_{\mathbf{1}-X/Y/\mathbf{1}-X/Y^{\bullet-}}$ within 40 mV of each other and thus the reduction is not subject to the same substituent effect as the other azines. **1**-4-NO_2/4-NO_2 exhibits an E° at a similar potential, but is a two-electron reversible wave with features indicative of a reduction system containing two localized, nonconjugated redox centers. The reduction potentials of all the aryl azines were correlated with Hammett σ parameters to look at variations in $E^{\circ}_{\mathbf{1}-X/Y/\mathbf{1}-X/Y^{\bullet-}}$ vs SCE as a function of substituent. The small ρ values in combination with the other electrochemical data provide support for single bond character of the N−N bond and evidence for a lack of strong electronic communication between the two aryl centers through the azomethine bonds, especially for those systems with electron-withdrawing groups.

Introduction

Azines are a class of compound that undergo a wide variety of chemical processes and have interesting chemical properties. Among their useful properties, azines are receiving increased interest for their potential in bond formation reactions,[1−4] their biological properties,[5] in the design of liquid crystals,[6−13] and other material applications.[14−20] Azines and pyridyl-substituted azines have been used extensively as ligands for the design and synthesis of novel organometallic compounds.[21−29] Sur-

---

* To whom correspondence should be addressed. Tel: 519-661-2111 ext. 86319. Fax: 519-661-3022.

(1) Schweizer, E. E.; Cao, Z.; Rheingold, A. L.; Bruch, M. *J. Org. Chem.* **1993**, *58*, 4339−4345.

(2) Marek, R.; St′astná-Sedlácková, I.; Tousek, J.; Marek, J.; Potácek, M. *Bull. Soc. Chim. Belg.* **1997**, *106*, 645−649.

(3) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 321−328.

(4) Wagner-Jauregg, T. *Synthesis* **1976**, 349−373.

(5) Khodair, A. I.; Bertrand, P. *Tetrahedron* **1998**, *54*, 4859−4872.

(6) Sereda, S. V.; Antipin, M. Y.; Timofeeva, T. V.; Struchkov, Y. T. *Sov. Phys. Crystallogr.* **1988**, *33*, 66−70.

(7) Astheimer, H.; Walz, L.; Haase, W.; Loub, J.; Müller, H. J.; Gallardo, M. *Mol. Cryst. Liq. Cryst.* **1985**, *131*, 343−351.

(8) Centore, R.; Panunzi, B.; Tuzi, A. *Z. Kristallog.* **1996**, *211*, 31−38.

(9) Centore, R.; Garzillo, C. *J. Chem. Soc., Perkin Trans. 2* **1997**, *2*, 79−84.

(10) Espinet, P.; Etxebarria, J.; Marcos, M.; Péres, J.; Remón, A.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1065−1066.

(11) Melendez, E.; Serrano, J. L. *Mol. Cryst. Liq. Cryst.* **1983**, *91*, 173−185.

(12) Marcos, M.; Melendez, E.; Ros, B.; Serrano, J. L. *Can. J. Chem.* **1985**, *63*, 2922−2925.

(13) Marcos, M.; Melendez, E.; Serrano, J. L. *Mol. Cryst. Liq. Cryst.* **1983**, *91*, 157−172.

(14) Centore, R.; Panunzi, B.; Roviello, A.; Sirigu, A.; Villano, P. *Mol. Cryst. Liq. Cryst.* **1996**, *275*, 107−120.

(15) Hauer, C. R.; King, G. S.; McCool, E. L.; Euler, W. B.; Ferrara, J. D.; Youngs, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 5760−5765.

(16) Dudis, D. S.; Yeates, A. T.; Kost, D.; Smith, D. A.; Medrano, J. *J. Am. Chem. Soc.* **1993**, *115*, 8770−8774.

(17) Kesslen, E. C.; Euler, W. B. *Tetrahedron Lett.* **1995**, *36*, 4725−4728.

(18) Euler, W. B. In *Handbook of Organic Conductive Molecules and Polymers: Vol 2. Conductive Polymers: Synthesis and Electrical Properties*; Wiley: New York, 1997; pp 719−740.

(19) Osborne, A. G.; Silva, M. W. d.; Hursthouse, M. B.; Malik, K. M. A.; Opromolla, G.; Zanello, P. *J. Organomet. Chem.* **1996**, *516*, 167−176.

(20) Amari, C.; Pelizzi, C.; Predieri, G.; Destri, S.; Porzio, W.; Einsiedel, H.; Menges, B.; Mittler-Neher, S. *J. Mater. Chem.* **1996**, *6*, 1319−1324.

(21) Granifo, J.; Vargas, M. E.; Dodsworth, E. S.; Farrar, D. H.; Fielder, S. S.; Lever, A. B. P. *J. Chem. Soc., Dalton Trans.* **1996**, 4369−4378.

(22) Cedar, R. M.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1351−1358.

(23) Shaw, B. L.; Thornton-Pett, M.; Vessey, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 1697−1707.

(24) Asselt, R. v.; Elsevier, C. J.; Amatore, C.; Jutand, A. *Organomet.* **1997**, *16*, 317−328.

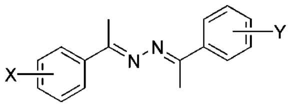
(25) Shaw, B. L.; Perera, S. D.; Shenton, D. J.; Thornton-Pett, M. *Inorg. Chim. Acta* **1998**, *270*, 312−325.

(26) Shaw, B. L.; Iranpoor, N.; Perera, S. D.; Thornton-Pett, M.; Vessey, J. D. *J. Chem. Soc., Dalton Trans.* **1998**, 1885−1891.

(27) Zippel, T.; Arndt, P.; Ohff, A.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 4429−4437.

10.1021/jo0056287 CCC: \$20.00

prisingly, despite the synthetic utility and potential material applications very little is known about their electronic properties.

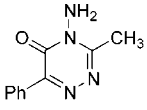


1-X/Y

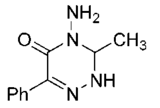
Azines are 2,3-diaza derivatives of butadienes (>C=N-N=C<). The two imine bonds that make up the azine moiety can be considered polar acceptor groups oriented in opposite directions since they are joined by an N−N bond. This characteristic of azines, when bonded to two aryl rings that contain a donor and an acceptor group, respectively, suggested that they would make ideal candidates for NLO materials. Over the past decade, Glaser and co-workers have been interested in the possible linear and nonlinear optical properties of these systems.[30−39] To this end, they have surveyed a large number of symmetric and asymmetrical acetophenone azines (**1**) with donor and acceptor groups in the para positions of the aryl rings and have been examining their molecular structure and crystal packing features. In the course of their survey, they have recently reported a number of prototypical aryl azines that exhibit some of the features that may provide the NLO response.[35,37]

The structure of aryl azines appears to be ideally suited for complete conjugation throughout the entire molecule because of the extended π system. This question of azine conjugation is being addressed both experimentally and theoretically.[8,9,30−40] One of the conditions for complete conjugation is the planarity of the molecule both in the azine spacer as well as the aryl rings. Glaser and co-workers reported the solid-state structures of a wide variety of azines, including the acetophenone azines, paying particular attention to the their extent of conjugation and to the geometry around the C=N-N=C bonds. Their work showed that in the solid state there is significant structural variation in the geometry around the C=N-N=C bonds as a function of both the steric and electronic properties of the substituents on the azine moiety. In general, the C=N-N=C bonds assume gauche conformations resulting in a lack of planarity, and suggesting poor conjugative interactions. For some systems, particularly symmetric aryl azines with strong electron donating or withdrawing groups, that molecule assumes a trans conformation about the azine moiety having the expected 180° torsion angle. Theoretical calculations have shown that the potential energy surface is quite shallow in the region of $120° < \tau < 180°$, and thus, the energy difference for conversion between the gauche and trans conformations is relatively small.[35,36] The data also showed that there is significant twisting of the aryl groups out of the best plane of the azine that also suggests poor conjugative interactions. Deviation in the observed torsion angles and the twisting of the phenyl rings is possibly the result of crystal packing effects. As well as the extensive investigation of the orientation of the azine molecules, Glaser also has examined the bond lengths in an attempt to find evidence for conjugation. By examining possible resonance structures of the symmetric and asymmetric acetophenone azines, he has identified selected bonds, which should be affected if any significant conjugation were present. However, the conclusion from their extensive X-ray analyses, including the conformational properties about the N−N and Ar−C bonds, bond length analysis and theoretical studies showed that there is no conjugation apparent. In total, although the C=N-N=C spacer appears to have the structural elements necessary to make it a good conjugation bridge, Glaser concludes that the azine unit is in fact a “conjugation stopper” at least in the solid state.[35,37]

Our interest lies in whether the lack of conjugation observed in the solid state is also present in solution, where the molecules have much more conformational flexibility. While the redox properties of azines have been studied in the past,[19,41−45] to date there has been no systematic examination of the electrochemical properties of a series of related azines. In an early electrochemical study, the reduction potential of the azine system C_6H_5-CH=N−N=CH-C_6H_5 was reported to be identical to that of the corresponding hydrazone, C_6H_5-CH_2-NH-N=CH-C_6H_5, suggesting a lack of conjugation in the former.[45] Zuman and co-workers more recently reported the aqueous redox properties of a number of triazine derivatives that contain a cyclic azine moiety.[46−48] Of their important results, which examine the irreversible reduction of the protonated forms of the azine in protic solvents, one pertinent to this question is illustrated by the reduction of the herbicide metamitron.[46] The first reduction wave



metamitron



2,3-dihydrometamitron

---

(28) Granifo, J.; Vega, A.; Garland, M. T. *Polyhedron* **1998**, *17*, 1729−1733.

(29) Edwards, D. A.; Hoskins, G. M.; Mahon, M. F.; Molloy, K. C.; Rudolph, G. R. G. *Polyhedron* **1998**, *17*, 2321−2326.

(30) Chen, G. S.; Anthamatten, M.; Barnes, C. L.; Glaser, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *34*, 1081−1084.

(31) Chen, G. S.; Anthamatten, M.; Barnes, C. L.; Glaser, R. *J. Org. Chem.* **1994**, *59*, 4336−4340.

(32) Chen, G. S.; Wilbur, J. K.; Barnes, C. L.; Glaser, R. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2311−2317.

(33) Glaser, R.; Chen, G. S.; Barnes, C. L. *J. Org. Chem.* **1993**, *58*, 7446−7455.

(34) Glaser, R.; Chen, G. S.; Anthamatten, M.; Barnes, C. L. *J. Chem. Perkin Trans. 2* **1995**, 1449−1458.

(35) Glaser, R.; Chen, G. S. *J. Comput. Chem.* **1998**, *19*, 1130−1140.

(36) Glaser, R.; Lewis, M.; Wu, Z. *J. Mol. Model* **2000**, *6*, 86−98.

(37) Lewis, M.; Barnes, C. L.; Glaser, R. *Can. J. Chem.* **1998**, *76*, 1371−1378.

(38) Lewis, M.; Barnes, C. L.; Hathaway, B. A.; Glaser, R. *Acta Crystallogr.* **1999**, *C55*, 975−978.

(39) Lewis, M.; Barnes, C. L.; Glaser, R. *Acta Crystallogr.* **2000**, *C56*, 393−396.

(40) Kesslen, E. C.; Euler, W. B.; Foxman, B. M. *Chem. Mater.* **1999**, *11*, 336−340.

(41) Wiberg, K. B.; Lewis, T. P. *J. Am. Chem. Soc.* **1970**, *92*, 7154−7160.

(42) Nieto, M. A. G.; Castro, M. D. L. d.; Valcarcel, M. *Electrochim. Acta* **1983**, *28*, 1725−1732.

(43) Barnes, J. H.; Triebe, F. M.; Hawley, M. D. *J. Electroanal. Chem.* **1982**, *139*, 395−411.

(44) Handoo, K. L.; Handoo, S. K. *Ind. J. Chem.* **1980**, *19B*, 684−687.

(45) Lund, H. *Acta Chem. Scand.* **1959**, *13*, 249−267.

(46) Ludvík, J.; Riedl, F.; Liska, F.; Zuman, P. *J. Electroanal. Chem.* **1998**, *457*, 177−190.

(47) (a) Riedl, F.; Ludvík, J.; Liska, F.; Zuman, P. *J. Heterocycl. Chem.* **1996**, *33*, 2063−2064. (b) Privman, M.; Zuman, P. *J. Electroanal. Chem.* **1998**, *455*, 235−246.

(48) Sauro, V. A.; Pitters, J. L.; Workentin, M. S. Cathodic Reduction of Aryl Azines: Evidence for Weak Conjugation. In *Organic Electrochemistry: Manuel L. Baizer Award Symposium in Honor of J. Simonet and J. W. P. Utley (4th)*; Fry, A., Steckhan, E., Matsumura, Y., Eds.; Electrochemical Society: Pennington, NJ, 2000; p 156.

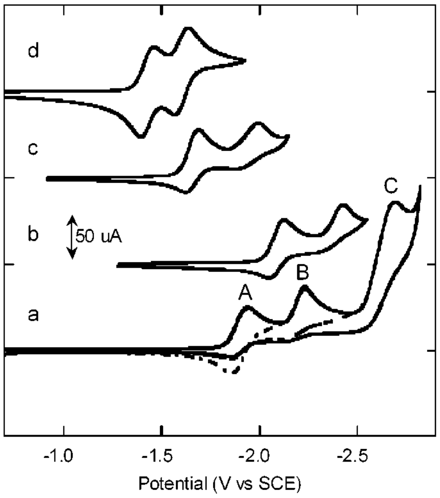


Figure 1. Cyclic voltammograms of selected azines measured in 0.1 M TEAP/acetonitrile at 0.1 V s^{-1}: (a) **1**-3-OCH_3/3-OCH_3 showing the complete CV; (b) **1**-4-OCH_3/4-OCH_3; (c) **1**-4-OCH_3/4-CN; (d) **1**-4-CN/4-CN showing only the first two reduction waves. In the CV for **1**-3-OCH_3/3-OCH_3 (a), the dashed lines are the CVs when the potential is switched between A, B and B, C.

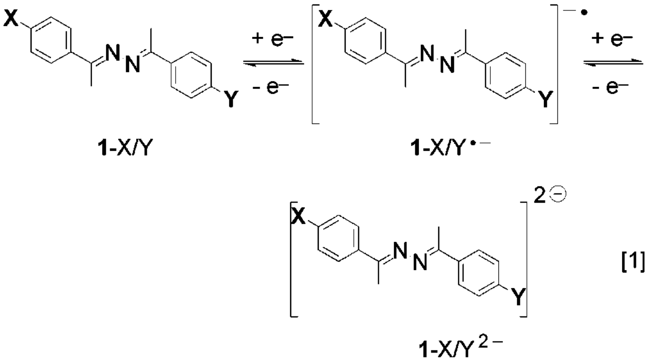
of metamitron is coincident with the reduction of 2,3-dihydrometamitron and is thought to involve the reduction of the 1,6-imine bond. Since the reduction of the azine bond in metamitron is coincident with its dihydro counterpart, this indicates a lack of conjugation and thus a lack of electronic communication, between the two azomethine bonds of the azine moiety in metamitron in aqueous solution.[49]

To properly exploit the chemistry of azines, an understanding of the electronic factors that affect their stability and reactivity is required. Central to this issue is to understand the extent of conjugation through the C=N-N=C. We now report the electrochemical redox properties of a series of structurally related substituted acetophenone azines ((**1**-X/Y, where X and Y are 4-NO_2, 4-CN, H, 3-OCH_3, 4-OCH_3, 4-CH_3, and 4-$N(CH_3)_2$) in aprotic solvents. Both symmetrical (X = Y) and asymmetrical (X ≠ Y) aryl azines were examined, including many examined in the solid state by Glaser and co-workers, to determine if the lack of conjugation found in the solid-state manifests itself in the solution-phase redox properties.

Results and Discussion

The acetophenone azines **1**-X/Y required for this study were prepared by published procedures, or modifications of published procedures; full details are in the Experimental Section or the Supporting Information. The electrochemical behavior of the series of symmetrical and unsymmetrical aryl-substituted acetophenone azines (**1**-X/Y) was studied in acetonitrile (MeCN) and *N*,*N*-dimethylformamide (DMF), using cyclic voltammetry (CV). All the nonnitro containing azines showed similar cyclic voltammetric features. Figure 1a shows a representative cyclic voltammogram for **1**-3-OCH_3/3-OCH_3. The characteristic voltammetric features include a single electron cathodic wave that is reversible at all scan rates investigated (A), followed at more negative potentials by a second single electron cathodic wave (B) where the reversibility depends on the scan rate. Examples of the reduction of other **1**-X/Y appear in Figure 1b–d. The first two reduction waves represent the successive reduction of the corresponding azine to its radical anion (**1**-$X/Y^{\bullet-}$) and then its dianion (**1**-X/Y^{2-}), respectively. In all cases the formation of **1**-$X/Y^{\bullet-}$ is completely chemically reversible.

For this series, standard reduction potentials, $E^\circ_{\mathbf{1}-X/Y/\mathbf{1}-X/Y^{\bullet-}}$, vary as a function of substituent and are summarized in Table 1. On the other hand, the reversibility of the formation of the dianion is substituent and scan rate dependent. The formation of the dianions of **1**-3-OCH_3/3-OCH_3, **1**-H/H, **1**-H/4-CH_3, **1**-H/4-OCH_3, **1**-4-CH_3/4-CH_3, **1**-3-OCH_3/4-OCH_3, **1**-4-CN/4-$N(CH_3)_2$, and **1**-4-OCH_3/4-OCH_3 were not reversible on the CV time scale up to 50 V s^{-1} in either solvent. In the cases of **1**-4-CN/4-CN, **1**-4-OCH_3/4-NO_2, **1**-3-OCH_3/4-NO_2, **1**-4-CN/3-OCH_3, **1**-H/3-OCH_3, and **1**-H/4-NO_2, the dianions are sufficiently stable and provide a value for $E^\circ_{\mathbf{1}-X/Y^{\bullet-}/\mathbf{1}-X/Y^{2-}}$. The dianions of **1**-H/4-CN and **1**-4-OCH_3/4-CN are sufficiently stable only at faster scan rates in acetonitrile, but at all scan rates in DMF while the dianion of **1**-4-CN/4-$N(CH_3)_2$ is sufficiently stable only at faster scan rates in both solvents. Table 1 also provides $E^\circ_{\mathbf{1}-X/Y^{\bullet-}/\mathbf{1}-X/Y^{2-}}$or E_p values depending on the reversibility described above. We believe that the lack of reversibility of certain dianions indicates that they are sufficiently basic to abstract a proton from solvent molecules or, more likely, residual water present in the “dry” solvent ([H_2O] estimated to be <0.1 mM in acetonitrile). The cathodic wave labeled C (Figure 1a) is a multielectron wave (~$2e^-$) caused by the subsequent reduction of the products from the protonated dianion (see below) presumably to form amines as the ultimate products.[50] In some cases, the multielectron wave is not observed, since it occurs at too negative a potential and occurs into the solvent discharge.



CVs showing the reversible reduction of **1**-X/Y to **1**-$X/Y^{\bullet-}$ at 100 mV s^{-1} are shown in Figure 2, which illustrates the large substituent effect on the single-electron reduction (values differ by more than 1.1 V); the more electron-withdrawing the substituent the easier the azine is to reduce and the more positive the E° value. Each **1**-X/Y shows a single electron, reversible wave, based on the $i_p/\sqrt{\nu}$ value in comparison with ferrocene as a standard.

The potentials ($E^\circ_{\mathbf{1}-X/Y^{\bullet-}/\mathbf{1}-X/Y^{2-}}$ or E_p) for the second reduction follow the same trend with substituent donating and withdrawing ability (see Table 1). The substituent effect is slightly larger for the secondwave with

---

(49) Zuman, P.; Ludvik, J. *Tetrahedron Lett.* **2000**, *41*, 7851–7853.

(50) Soucaze-Guillous, B.; Lund, H. *Acta Chem. Scand.* **1997**, *51*, 354–358.

Table 1. Electrochemical Data for the Reduction of Azines in 0.1 M TEAP/Acetonitrile Solution (Data in Parentheses Are Values in 0.1 M TEAP/DMF Solution)

1-X/Y				
X	Y	$E°_{1/1^{\bullet-}}$[a] (V)	$E°_{/1^{\bullet-}/1^{2-}}$[a,c] (V)	$E_{p(C)}$[a,g] (V)
4-NO_2	4-NO_2	−0.952[b] (−0.934)[b]		
4-NO_2	3-OCH_3	−0.977 (−0.970)	−1.482[d] (−1.502)[d]	
4-NO_2	H	−0.983 (−0.973)	−1.494[d] (−1.513)[d]	
4-NO_2	4-OCH_3	−0.999 (−0.978)	−1.545[d] (−1.565)[d]	
4-CN	4-CN	−1.426 (−1.367)	−1.602[d] (−1.597)[d]	−2.665 (−2.775)
4-CN	3-OCH_3	−1.593 (−1.544)	−1.893[d] (−1.912)[d]	−2.450 (−2.589)
4-CN	H	−1.602 (−1.550)	−1.915[e] (−1.926)[d]	−2.441 (−2.623)
4-CN	4-OCH_3	−1.648 (−1.595)	−1.973[e] (−2.002)[d]	−2.455 (−2.735)
4-CN	4-$N(CH_3)_2$	−1.669 (−1.632)	−2.011[e] (−2.035)[e]	−2.431 (−2.446)
H	H	−1.932 (−1.891)	−2.252[f] (−2.290)[f]	−2.680 (−2.772)
H	4-CH_3	−1.965 (−1.929)	−2.331[f] (−2.343)[f]	−2.743 (−)[h]
H	4-OCH_3	−2.004 (−1.969)	−2.320[f] (−2.355)[f]	−[h] (−2.781)
H	4-$N(CH_3)_2$	−2.054 (−2.026)	−2.353[f] (−2.416)[f]	−[h] (−)[h]
4-CH_3	4-CH_3	−2.005 (−1.972)	−2.371[f] (−2.402)[f]	−2.723 (−)[h]
3-OCH_3	3-OCH_3	−1.898 (−1.867)	−2.231[f] (−2.268)[f]	−2.692 (−)[h]
3-OCH_3	H	−1.912 (−1.876)	−2.264[f] (−2.329)[e]	−2.684 (−)[h]
3-OCH_3	4-OCH_3	−1.983 (−1.957)	−2.313[f] (−2.370)[f]	−[h] (−)[h]
4-OCH_3	4-OCH_3	−2.088 (−2.059)	−2.430[f] (−2.462)[f]	−2.753 (−2.774)

[a] Reported in V versus SCE. [b] Not $E°$ for **1**-X/Y/**1**-X/$Y^{\bullet-}$, see text. [c] $E°$ unless noted. [d] Reversible at all scan rates. [e] Reversible only at faster scan rates. [f] Reported as peak potentials at 0.1 V s^{-1} scan rate. Irreversible up to 50 V s^{-1} scan rate. [g] Peak potential for the reduction of the protonated dianion at 0.1 V s^{-1} scan rate; see text. [h] The $E_{p(C)}$ for these compounds was obscured by the solvent cutoff.

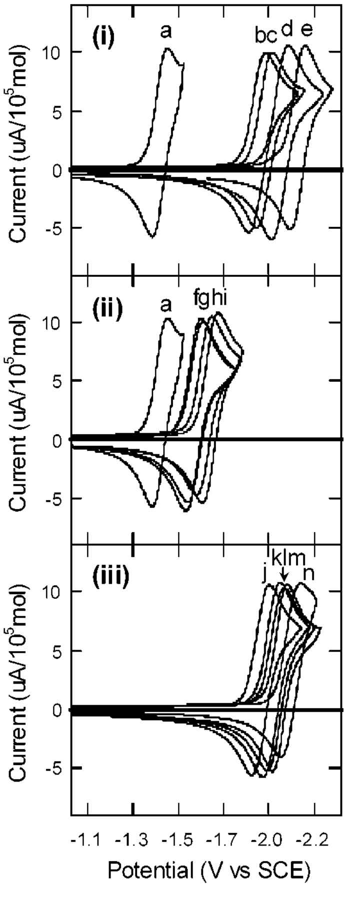


Figure 2. Cyclic voltammograms of the first reversible reduction waves for selected azines in 0.1 M TEAP/acetonitrile at 0.1 V s^{-1} scan rate: (a) **1**-4-CN/4-CN; (b) **1**-3-OCH_3/3-OCH_3; (c) **1**-H/H; (d) **1**-4-CH_3/4-CH_3; (e) **1**-4-OCH_3/4-OCH_3; (f) **1**-3-OCH_3/4-CN; (g) **1**-H/4-CN; (h) **1**-4-OCH_3/4-CN; (i) **1**-4-CN/4-$N(CH_3)_2$; (j) **1**-H/3-OCH_3; (k) **1**-H/4-CH_3; (l) **1**-3-OCH_3/4-OCH_3; (m) **1**-H/4-OCH_3; (n) **1**-H/4-$N(CH_3)_2$.

potentials differing by over 0.8 V through the series from **1**-4-CN/4-CN to **1**-4-OCH_3/4-OCH_3. Typical CVs are illustrated in Figure 1.

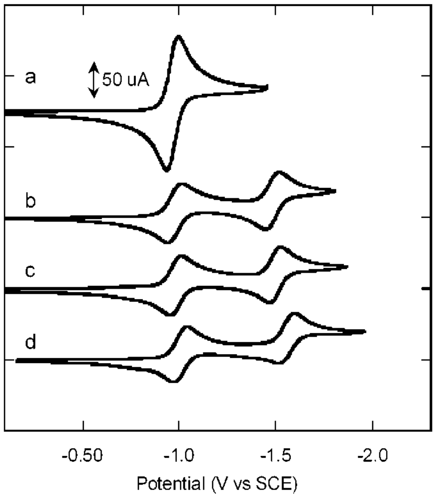


Figure 3. Cyclic voltammograms of the nitro-containing azines measured in 0.1 M TEAP/acetonitrile at 0.1 V s^{-1}: (a) **1**-4-NO_2/4-NO_2; (b) **1**-3-OCH_3/4-NO_2; (c) **1**-H/4-NO_2; (d) **1**-4-OCH_3/4-NO_2. Also shown is a second reversible reduction wave that is typical for all of the nitro containing azines except for **1**-4-NO_2/4-NO_2.

The nitro-containing azines deviate from the abovementioned behavior. The nitro-substituted azines, with the exception of **1**-4-NO_2/4-NO_2, exhibit single electron waves that have standard potentials within 40 mV of each other (see Figure 3). **1**-4-NO_2/4-NO_2 exhibits a standard potential at a similar potential but is a two-electron reversible wave. The reduction wave for the **1**-4-NO_2/4-NO_2 has the same peak parameters ($\Delta E_p = 59$ mV at 100 mV s^{-1}) as a reversible one-electron-transfer reduction with the exception that the peak current is twice the height. The characteristics exhibited by **1**-4-NO_2/4-NO_2 are indicative of a reduction system containing two localized, nonconjugated redox centers.[51] This suggests that reduction occurs at two independent centers roughly simultaneously and the observed reduction

---

(51) Bott, A. W. *Current Separations* **1997**, *16*, 61−66.

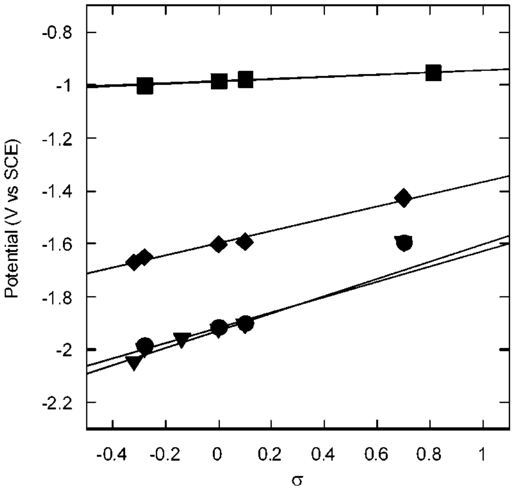


Figure 4. Hammett-type plot of σ versus $E°_{1-XY/1-XY^{\bullet-}}$ measured in 0.1 M TEAP/acetonitrile solution at 0.1 V s^{-1}. The ■, ◆, ▼, and ● are the data for the **1**-4-NO$_2$/Y, **1**-4-CN/Y, **1**-H/Y, and **1**-3-OCH$_3$/Y azines, respectively. Hammett σ values: 4-CN = 0.7, 4-NO$_2$ = 0.81, H = 0, 4-OCH$_3$ = −0.28, 4-CH$_3$ = −0.14, 3-OCH$_3$ = 0.1, 4-N(CH$_3$)$_2$ = −0.32.

wave is the product of two independent single-electron transfers which occur at the same reduction potential ($\Delta E°$ ca. 35 mV). The nitro-containing azines also show a second one-electron reduction wave except for **1**-4-NO$_2$/4-NO$_2$ that does not show a second reduction wave under the conditions of our experiment (vide supra). A summary of the electrochemical data appears in Table 1.

The reduction potentials of the aryl azines can be correlated with Hammett σ parameters to examine variations in $E°_{1-X/Y/1-X/Y^{\bullet-}}$ as a function of substituent; this is shown in Figure 4.[52] The plot shows distinct correlations for series of **1**-X/Y where one of the substituents is held constant and the other is varied: **1**-4-NO$_2$/Y, **1**-4-CN/Y, **1**-H/Y, and **1**-3-OCH$_3$/Y. For **1**-4-NO$_2$/Y, the $\rho^{4-NO_2/Y}$ value equals 0.04 V, essentially indicating no substituent effect. In addition, the $E°_{1-X/Y/1-X/Y^{\bullet-}}$ values are all approximately equal to −1 V vs SCE, roughly the same potential as nitrobenzene in the same solvents (−1.1 V vs SCE). These observations suggest that the reduction is localized on the NO$_2$ group and not at one of the azine C=N imine double bonds. In other words, the reduction of the nitro-substituted azines is behaving like substituted aryl nitro groups, as opposed to nitro-substituted aryl azines.

The second correlation is for the series **1**-4-CN/Y. Here, $\rho^{4-CN/Y} = 0.23$ V, suggesting a modest variation as a function of substituent. The last correlations shown are for the remaining azines. For these systems the ρ values are larger ($\rho^{H/Y} = 0.41$ V and $\rho^{3-OCH_3/Y} = 0.39$ V) and would suggest a greater substituent effect. In fact, we believe that these values are unnaturally high since the position of reduction changes as the Y substituent is changed. Product studies (see below) indicate that reduction takes place preferentially on the imine unit (Ar(CH$_3$)C=NX) closest to the most electron-withdrawing aryl substituent and this acts to attenuate the ρ value. For example, in the **1**-H/Y series the position of reduction on the molecule changes as we proceed from **1**-4-CN/H to **1**-4-N(CH$_3$)$_2$/H; in the former it is the NC-C$_6$H$_4$-(CH$_3$)C=N-X unit that is reduced, whereas in the latter reduction occurs on the C$_6$H$_5$-(CH$_3$)C=N-X unit. Taking this into account (e.g., 4-CN substituents are not included in correlation for X = H, or 3-OCH$_3$), the ρ values are smaller ($\rho^{3-OCH_3/Y}$ 0.33 V and $\rho^{H/Y} = 0.29$ V, respectively), indicating again only a modest substituent effect on the reduction.

Similar plots for $E°_{1-X/Y^{\bullet-}/1-X/Y^{2-}}$ (reduction of the radical anion to the dianion) have higher ρ values for the electron withdrawing substituents, suggesting a greater substituent effect ($\rho_2{}^{4-NO_2/Y} = 0.17$; $\rho_2{}^{4-CN/Y} = 0.39$) but are similar for the electron donating series ($\rho_2{}^{H/Y} = 0.30$ V and $\rho_2{}^{3-OCH_3/Y} = 0.29$ V). This aspect will be addressed below.

The preferential site for reduction has been confirmed by constant potential electrolysis product studies from the reduction of **1**-X/Y in the presence of a proton donor, namely the nonnucleophilic acid 2,2,2-trifluoroethanol (TFE). Upon the addition of TFE the cathodic peak current of the first reduction wave (A) increases with increasing acid concentration with a concomitant decrease in the current of the second wave (B). The reversibility of the first wave also decreased. These voltammetric features are indicative of an ECE mechanism where 1-X/Y$^{\bullet-}$ is protonated by TFE to yield what we assume to be the benzylic type radical, which is quickly reduced since it has a reduction potential much more positive than the radical anion (Scheme 1). The resulting anion is then protonated to yield the corresponding hydrazone, **2**. This series of events causes the two original single electron reduction waves to merge into a single irreversible wave, twice its original current height, at high enough acid concentration. Accompanying the increase in peak current with increasing acid concentration, there is also a shift in peak potential to more positive values. This shift is related to the rate constant (k_{H+}) for protonation of the radical anion. Constant current and constant potential coulometric experiments performed in the presence of a large excess of acid, indicate that the number of electrons involved in the reduction of the azines is always 2 F mol^{-1}. Hydrogenation of **1**-X/Y in the presence of Pd catalysts adds one equivalent of H$_2$ to yield the corresponding hydrazone. The electrolyses produced only a single product for each azine, verified by HPLC analysis and co-injection of authentic samples prepared by the hydrogenation of the **1**-X/Y. The products from the bulk electrolysis or hydrogenation were not stable to hydrolysis and were used immediately for HPLC analysis with the minimum amount of exposure to the atmosphere. The hydrogenation products were sufficiently stable to allow for NMR and UV−vis spectral characterization. Spectra are consistent with products where a single azomethine unit is reduced. In the case of the asymmetrical azines, the reduction (either by H$_2$/Pd or electrochemical) occurs across the imine bond closest to the more electron withdrawing of the two aryl substituents (verified by NMR and HPLC co-injection). The hydrogenated product of **1**-4-CN/4-CN was stable enough to hydrolysis to perform an electrochemical experiment. The reduction observed for this compound matched those observed for the parent azine, in the presence of excess acid, except for the disappearance of the initial two electron irreversible wave.

The data for the reduction of neutral **1**-4-NO$_2$/Y, in particular **1**-4-NO$_2$/4-NO$_2$ provides compelling evidence for the lack of conjugation through the azine unit. What about for other substituents? We believe the small ρ

---

(52) Zuman, P. *Substituent Effects in Organic Polarography*; Plenum: New York, 1967.

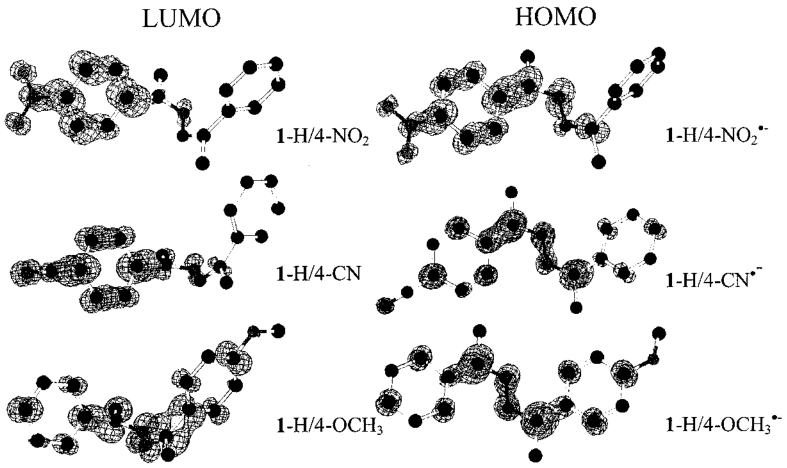
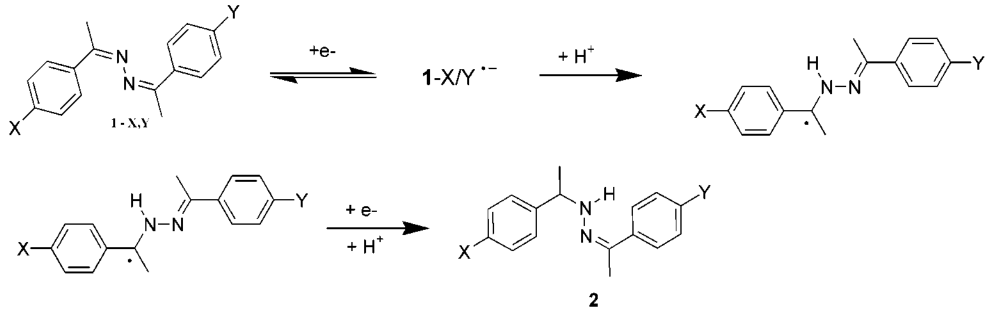


Figure 5. LUMO and HOMO of selected **1**-X/Y and **1**-X/Y$^{\bullet-}$, respectively, determined by semiempirical PM3 calculations.

Scheme 1



values from the data presented in Figure 4 provide qualitative evidence for the lack of strong electronic communication between the two aryl centers through the C=N−N=C bonds. A complete lack of any substituent effect would, of course, lead to reduction potentials for a particular series (e.g., **1**-4-CN/Y) being practically identical and a ρ value near zero, which is true only for **1**-4-NO_2/Y. The magnitudes of the substituent effects (and the resulting ρ values) for the other series are nonzero indicating some effect of the substituent. The magnitude is reasonable for transmission of the electronic effects either by inductive effects alone or with some conjugative effects; at present there is no clear way to determine the relative contribution from each. Of course, the extent of the latter may vary as a function of substituent if the geometry around the Ar-RC=N-N=CR-Ar or the nature of the LUMO varies.

The lack of strong conjugative interaction is consistent with the conclusions reached from X-ray crystallographic structural data for this series of azines, summarized in the Supporting Information, from our own data and that of Glaser's. The newer data is analogous to Glaser's and show that in the solid-state structure the majority of the **1**-X/Y have gauche geometries around the >C=N−N=C< moiety and that the bond lengths are not consistent with any extended conjugation (for example, no significant −N=N− character). Semiempirical calculations were also performed to qualitatively examine the structure of **1**-X/Y.[53] Calculated structures show a definite torsion angle about the N−N bond that is also apparent in the X-ray crystal structures (even when minimizations were started with the all planar structure), indicating that the geometry optimal for conjugation throughout the entire molecule is not preferred. Furthermore, the calculations also provide qualitative indication that the LUMO of the azines containing electron-withdrawing groups resides on the aryl moiety with no significant contribution on the azine >C=N-N=C< unit. In the case of the **1**-4-CN/Y and **1**-4-NO_2/Y, the LUMO is mainly localized on the NC-aryl or O_2N-aryl fragment; this is illustrated for **1**-H/4-NO_2 and **1**-H/4-CN in Figure 5. This provides further support for the conclusions from the electrochemical studies. For **1**-X/Y containing more electron-donating substituents the LUMO is more delocalized, but still has substantial contributions on the aryl moiety (for example see **1**-H/4-OCH_3 in Figure 5). In these cases, there is more likelihood for some extended conjugation, as is also suggested in the more substantial substituent effect on the redox properties.

In contrast to **1**-X/Y, the semiempirical calculations of **1**-X/Y$^{\bullet-}$ indicate that the molecules adopt a more planar configuration and that the HOMO is more highly delocalized with a significant contribution on the C=N-N=C fragment. Qualitatively, this provides support that **1**-X/Y$^{\bullet-}$ assume a geometry that is more capable of conjugation than the parent azines, which would provide a larger substituent effect on the second reduction, as is observed. For the reduction of the radical anions the effects of the substituents appear to be additive, with the E_p values correlating with the sum of the substituent parameters. This is expected for complete conjugation.[52] To further examine the characteristics of the **1**-X/Y$^{\bullet-}$, the UV−vis spectra of each of the radical anions were measured. Each radical anion is highly colored. Representative UV−vis spectra of **1**-X/Y$^{\bullet-}$ are shown in Figure 6 and the λ_{max} are summarized in Table 2. These results coupled with the

---

(53) *Hyperchem*; Hypercube, Inc.: Gainsville, FL, 1996.

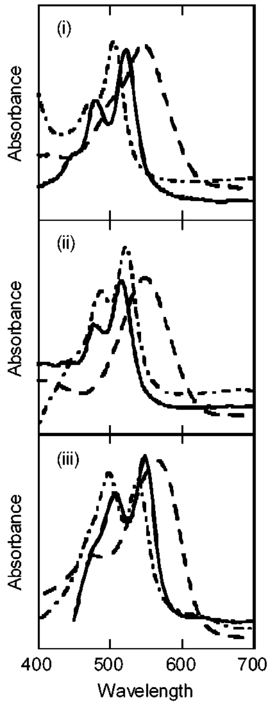


Figure 6. UV−vis spectra of selected **1**-X/Y$^{\bullet-}$ in 0.1 M TEAP/DMF solution: (• - •) are for **1**-4-OCH$_3$/4-OCH$_3$, **1**-H/4-N(CH$_3$)$_2$, and **1**-4-CN/4-OCH$_3$, (solid line) are for **1**-3-OCH$_3$/3-OCH$_3$, **1**-H/H, and **1**-4-CN/4-N(CH$_3$)$_2$, (dash) are for **1**-4-CN/3-OCH$_3$, **1**-H/4-CN, and **1**-4-CN/4-CN in (i), (ii), and (iii), respectively.

Table 2. UV−Vis Spectral Data for 1-X/Y$^{\bullet-}$ in 0.1 M TEAP/DMF Solution

1-X/Y			
X	Y	λ_{max}/nm	λ/nm
4-CN	4-CN	564	468
4-CN	3-OCH$_3$	547	504
4-CN	H	548	
4-CN	4-OCH$_3$	538	497, 467
4-CN	4-N(CH$_3$)$_2$	547	509, 475
H	H	515	478
H	4-CH$_3$	514	482, 447
H	4-OCH$_3$	510	481, 447
H	4-N(CH$_3$)$_2$	522	487
4-CH$_3$	4-CH$_3$	514	479, 447
3-OCH$_3$	3-OCH$_3$	522	482, 447
3-OCH$_3$	H	518	478, 447
3-OCH$_3$	4-OCH$_3$	515	482, 447
4-OCH$_3$	4-OCH$_3$	504	471

larger substituent effect on $E^\circ_{\mathbf{1}-\mathrm{X/Y}^{\bullet-}/\mathbf{1}-\mathrm{X/Y}^{2-}}$ suggest that there is more extensive conjugation in the radical anion than in the neutral species.

Based on Glaser and co-worker's studies of the solid-state structures of **1**-X/Y they have coined the term "conjugation-stopper" to describe the azine unit; our electrochemical data supports this analogy. Of course, the dihedral angle around the C═N-N═C and thus the extent of conjugation may vary somewhat as a function of substituent; this is currently difficult to interpret since the geometry in solution is much more fluxional, especially around the N−N bond. Limited delocalization may also occur by interactions through the nitrogen lone pairs and not directly through the π system. Since the electrochemical studies do show a small substituent effect on the reduction potentials, the azine unit may not be a complete "conjugation stopper" in solution, but the extent of conjugation is limited. Thus, the limited conjugation in >C═N-N═C< units observed in the solid state manifests itself in solution. This undoubtedly plays a role in the chemistry and application of this functional group. In contrast, the corresponding azine radical anions exhibit a larger substituent effect on their reduction. This, along with the qualititative semiempirical calculations and absorption spectroscopy, may reflect a stronger conjugative interaction. This aspect is currently being explored.

Experimental Section

Materials. All chemicals used were purchased from Aldrich and used as received unless otherwise stated. Acetonitrile was distilled over calcium hydride and then immediately cycled through activated alumina just prior to use. *N*,*N*-Dimethylformamide (DMF) was stored over NaHCO$_3$ and then distilled under reduced pressure over calcium hydride just prior to use. Argon was flushed over the acetonitrile and DMF during the transfers into the electrochemical and absorption spectroscopy cells. Tetraethylammonium perchlorate (Kodak) was recrystallized three times and dried under vacuum at 60 °C prior to use and stored in a vacuum desiccator. Ferrocene was sublimed once before use. NMR spectra were recorded on a Varian Gemini 300 MHz or Varian Mercury 400 MHz instrument. All chemical shifts are reported in parts per million downfield from tetramethylsilane. Melting points were recorded using a Gallenkamp melting point apparatus and are uncorrected. IR data was recorded on a Perkin-Elmer System 2000 FT-IR. Mass spectra analysis was performed with a Finnigan MAT 8200 mass-data system. Gas chromatography analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 10 m HP5 column and an FID detector. UV−vis spectra were recorded on a Varian Cary 100 spectrometer.

Electrochemistry: Cyclic Voltammetry. Experiments were performed using either a Princeton Applied Research (PAR) 283 or 263 potentiostat interfaced to a personal computer. PAR M270 software was used to conduct the experiments as well as analyze the derived data. Measurements were conducted in an all-glass cell kept at 25 °C. All glassware was dried in an oven and assembled hot while flushing with argon. The working electrode was glassy carbon (Tokai), and the counter electrode was a platinum flag. The reference electrode was a silver wire housed in a glass tube sealed with a porous ceramic tip and filled with a 0.1 M solution of tetraethylammonium perchlorate (TEAP). The same reference electrode was used in all experiments. Concentrations of 2 mM of azine in 0.1 M TEAP in acetonitrile or DMF were used. Ferrocene was used in all experiments as an internal reference, and potentials are referenced in turn to the saturated calomel electrode ($E°$ = 0.449 V and 0.470 V vs SCE in MeCN and DMF, respectively). Positive feedback IR compensation was used in all experiments to minimize the effects of uncompensated solution resistance. **Constant Current Coulometry.** 2 mM of azine was dissolved in 25 mL of 0.1 M TEAP/acetonitrile solution at 25 °C. A flow of argon was bubbled into the solution continuously to prevent oxygen from entering the cell. The solution was vigorously stirred throughout the experiment. The working electrode was a mercury pool. The counter electrode was a platinum coil separated from the bulk solution by a 2 mm thick layer of activated alumina and a sintered glass disk. A constant current (25 mA) was applied to the cell using a Hewlett-Packard 6212B power supply, monitored by a Fluke 8000A digital multimeter, for various amounts of time. The experiment was monitored by CV employing a glassy carbon working electrode. **Constant Potential Coulometry.** Typically, 30 mg of azine was dissolved in an appropriate amount of 0.1 M TEAP/acetonitrile solution at 25 °C. Argon was continuously bubbled to eliminate oxygen and the solution was vigorously stirred. The working electrode was a mercury pool. The counter electrode was a platinum coil separated from the bulk solution by a 2 mm thick layer of activated alumina and a sintered glass disk. The appropriate constant potential was applied using either a Princeton Applied Research (PAR) 283 or 263 potentiostat.

Bulk Electrolysis and HPLC Analysis. Bulk electrolysis was performed as per constant potential coulometry using approximately 10−12 mg of **1**-X/Y and a large excess of 2,2,2-trifluoroethanol (TFE) in 25 mL of 0.1 M TEAP/acetonitrile solution at 25 °C. Once electrolysis was complete, 100 μL was removed from the electrochemical cell and diluted to 2 mL with acetonitrile. The resultant solution was analyzed using a Waters Millipore HPLC on a C18 reversed-phase column with 20:80 water, acetonitrile mixture as eluent. The results were compared to hydrogenated samples of selected **1**-X/Y.

Hydrogenation and HPLC Analysis.[54] A 10−12 mg sample of azine was dissolved in a solution of DMF containing a catalytic amount of palladium black. One equivalent of hydrogen gas was added in a sealed hydrogenation apparatus at atmospheric pressure. A 100 μL portion of the solution was filtered and diluted to 2 mL with acetonitrile. The resultant solution was analyzed using a Waters Millipore HPLC on a C18 reverse phase column with 20:80 water, acetonitrile mixture as eluent. The results were compared to the bulk electrolysis samples of selected **1**-X/Y.

Synthesis of Acetophenone Azines. The symmetric azines **1**-4-CN/4-CN, **1**-3-OCH_3/3-OCH_3, **1**-4-OCH_3/4-OCH_3, **1**-4-CH_3/4-CH_3, **1**-4-NO_2/4-NO_2, and **1**-H/H were synthesized according to a published procedure and the spectral characterization and other physical data matched that previously reported.[55] The asymmetrical azines were synthesized by adding the appropriate substituted acetophenone to the corresponding substituted acetophenone(diethoxyphosphinyl)-hydrazone in benzene/NaH. Both the preparation of the substituted-acetophenone(diethoxyphosphinyl)hydrazone and **1**-X/Y were done according to the procedure of Chen et al. with some modification:[32]

The following **1**-X/Y are, to the best of our knowledge, either new compounds or compounds where the complete spectral data has not yet been reported. X-ray crystallographic data is also available for new compounds and is summarized in the Supporting Information.

4-Nitroacetophenone azine (1-H/4-NO_2): ^{1}H NMR (300 MHz) δ_H ($CDCl_3$) 2.31 (s, 3H), 2.34 (s, 3H), 7.42 (m, 3H), 7.90 (m, 2H), 8.05 (d, 2H), 8.25 (d, 2H); mp = 113−114 °C.

4-Cyanoacetophenone azine (1-H/4-CN): ^{1}H NMR (300 MHz) δ_H($CDCl_3$) 2.30 (s, 3H), 2.31 (s, 3H), 7.42 (m, 3H), 7.70 (d, 2H), 7.90 (m, 2H), 8.00 (d, 2H); mp = 132−134 °C.

4-Methoxyacetophenone azine (1-H/4-OCH_3)*:* ^{1}H NMR (300 MHz) δ_H ($CDCl_3$) 2.32 (s, 3H), 2.34 (s, 3H), 3.88 (s, 3H), 6.94 (d, 2H), 7.40 (m, 3H), 7.90 (m, 4H); mp = 134−136 °C.

4-Dimethylaminoacetophenone azine (1-H/4-$N(CH_3)_2$): ^{1}H NMR (400 MHz) δ_H ($CDCl_3$) 2.29 (s, 3H), 2.33 (s, 3H), 3.00 (s, 6H), 6.71 (d, 2H), 7.39 (m, 3H), 7.83 (d, 2H), 7.89 (m, 2H); mp = 146−147 °C.

3-Methoxyacetophenone azine (1-H/3-OCH_3): ^{1}H NMR (400 MHz) δ_H ($CDCl_3$) 2.28 (s, 3H), 2.29 (s, 3H), 3.89 (s, 3H), 6.96 (d, 1H), 7.32 (t, 1H), 7.42 (m, 4H), 7.50 (m, 1H), 7.89 (m, 2H); mp = 74−76 °C.

4-Methylacetophenone azine (1-H/4-CH_3): ^{1}H NMR (300 MHz) δ_H ($CDCl_3$) 2.29 (s, 3H) 2.30 (s, 3H), 2.38 (s, 3H), 7.21 (d, 2H), 7.40 (m, 3H), 7.79 (d, 2H), 7.88 (m, 2H); mp = 90−91 °C.

3,4′-Dimethoxyacetophenone azine (1-3-OCH_3/4-OCH_3): ^{1}H NMR (400 MHz) δ_H ($CDCl_3$) 2.28 (s, 3H), 2.29 (s, 3H), 3.84 (s, 3H), 3.85 (s, 3H), 6.94 (m, 3H), 7.31 (t, 1H), 7.43 (m, 1H), 7.50 (m, 1H), 7.86 (d, 2H); mp = 79−81 °C.

3-Methoxy-4′-nitroacetophenone azine (1-3-OCH_3/4-NO_2): ^{1}H NMR (300 MHz) δ_H ($CDCl_3$) 2.29 (s, 3H), 2.33 (s, 3H), 3.86 (s, 3H), 6.98 (m, 1H), 7.33 (t, 1H), 7.47 (m, 2H), 8.05 (d, 2H), 8.26 (d, 2H); mp = 88−90 °C.

3-Methoxy-4′-cyanoacetophenone azine (1-3-OCH_3/4-CN): ^{1}H NMR (300 MHz) δ_H ($CDCl_3$) 2.27 (s, 3H), 2.30 (s, 3H), 3.85 (s, 3H), 6.99 (m, 1H), 7.33 (t, 1H), 7.46 (m, 2H), 7.69 (d, 2H), 7.99 (d, 2H); mp = 85−87 °C.

3,3′-Dimethoxyacetophenone azine (1-3-OCH_3/3-OCH_3): ^{1}H NMR (300 MHz) δ_H ($CDCl_3$) 2.27 s, 6H), 3.85 (s, 6H), 6.95 (m, 2H), 7.32 (t, 2H), 7.45 (m, 6H); mp = 97−99 °C.

4-Cyano-4′-dimethylaminoacetophenone azine (1-4-CN/4-$N(CH_3)_2$): ^{1}H NMR (300 MHz) δ_H ($CDCl_3$) 2.29 (s, 3H), 2.35 (s, 3H), 3.01 (s, 6H), 6.71 (d, 2H), 7.67 (d, 2H), 7.84 (d, 2H), 7.99 (d, 2H); mp = 202−204 °C.

X-ray Crystallography. Single crystals of **1**-H/4-CN, **1**-H/4-OCH_3, **1**-H/4-NO_2, **1**-3-OCH_3/3-OCH_3, **1**-3-OCH_3/4-CN, and **1**-3-OCH_3/4-NO_2 were grown by slow evaporation of a concentrated solution of **1**-X/Y in an appropriate solvent. Crystals were mounted on a glass fiber. Data were collected on a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data sets. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other adsorption corrections were applied. The SHELXTL 5.1 (Sheldrick, G. M., Madison, WI) program package was used to solve the structures by direct methods, followed by successive difference Fouriers. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. X-ray data are given in the Supporting Information.

Acknowledgment. The financial support of the Natural Science and Engineering Research Council of Canada, Canadian Foundation for Innovation, ORCDF, and the University of Western Ontario (ADF) is appreciated. V.A.S. thanks the OGS program for a scholarship. Discussions with Professor P. Zuman about the relationship between our results and his examples of cyclic azines in aprotic solvents were beneficial.

Supporting Information Available: A complete Experimental Section, including spectral characterization of all new compounds and tables of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0056287

---

(54) Yoshino, K.; Ohkatsu, Y.; Tsuruta, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1738−1742.

(55) Cohen, S. G.; Groszos, S. J.; Sparrow, D. B. *J. Am. Chem. Soc.* **1950**, *72*, 3947−3951.