follows as closely as possible.[7] Condensation of 2,4-pentanedione (10 g, 0.01 mol) with benzaldehyde (5.3 g, 0.005 mol) in 70% ethanol, catalyzed by 1 mL of piperidine gave **3A** as a precipitate after a 3-day reaction period (8.1 g, 43% yield, mp 165–169 °C). Subsequent crops could be attained on concentration of the mother liquor. The crude product was recrystallized from hot benzene, giving white crystals, mp 173–174 °C. This melting point deteriorated on standing for several days, finally giving mp 165–168 °C, similar to the behavior reported by Knoevenagel.[7]

Extraction of the Enol 3B. A portion of the crude product (6.0 g) was dissolved in 30 mL of boiling benzene to give a yellow liquid. The hot benzene solution was then poured into a beaker and left to cool for about 12 h. White crystals precipitated on cooling. After 12 h the white crystals were filtered and washed with a small amount of benzene, giving **3A**, mp 173–174 °C. The filtrate from this benzene extraction was then evaporated on a steam bath until about three-fourths the original volume remained. The solution was set aside to cool for several days. After 3 days, fine white crystals appeared, although a rust-colored oil contaminated the crystals. The mixture was stirred for several hours to disperse the oil. The crude material was filtered and washed with a very small amount of 50% ethanol. The orangish filtrate from this was set aside. It was then evaporated until a dark brown oil remained. A small amount of water was added and the mixture warmed and stirred. This mixture was then left to cool with constant stirring; after several hours, crystals appeared. The NMR spectrum indicated that this second batch of crystals was the enol isomer **3B**, in particular, the characteristic peak at δ 16 (see Table II for other absorptions): IR 3520, 1705, 1630–1600 (chelated enolic C=C and C=O), and 1360 cm^{-1}. Freshly precipitated material (by adding hexane to a CCl_4 solution) had a mp of 112–114 °C, but aged crystals, even stored in the cold under nitrogen, displayed a mp of 162–164 °C. The yield in successful runs was approximately 1% in our hands, but most frequently, no enol at all was obtained. The yield could be improved by recycling aged **3A**.

Isolation of Enol Isomer 3C. The original filtrate from the mother liquor was set aside for about 1 month; after that time, the viscous rusty orange liquid was vigorously stirred and hexane added, whereupon crystals precipitated from the solution. These were filtered and washed with cold hexane, mp 122–123 °C (lit.[7] mp 125–126 °C). The NMR spectrum showed the characteristic enolic hydrogen but otherwise quite different peaks than **3B**: IR 3610, 3500, 1720, 1630–1590 (chelated enolic C=C and C=O), and 1360 cm^{-1}. The yield of this second enol was of the order of 3.5% in most successful runs, and this material appeared to be stable to storage conditions in the cold.

Spectral Determinations. The carbon-13 NMR spectra were taken on Varian XL-100 and on Bruker WB 360 instruments. The NMR of **3A** was taken in $CDCl_3$ while those of the enols **3B** and **3C** were taken in CCl_4 that had been treated with alumina or molecular sieves (3A). The proton NMR spectra were taken on Bruker WB 360 and Varian EM 390 instruments. The IR spectra were taken on a Perkin-Elmer PE 283 instrument; spectra were run in CCl_4 solution. The spectra were also taken as thin films on NaCl plates. The major difference observed was the lack of free OH peaks. For the NOE experiments, a typical sample was run as follows: the sample was dissolved in dry $CDCl_3$ (from a newly opened bottle with the solvent passed over Al_2O_3). Dry nitrogen was passed through the solution until at least half of the original volume had evaporated. Me_4Si was added and nitrogen passed over just before sealing with the NMR tube cap. NOE experiments were done on the Varian EM 390. Later two-dimensional NOE runs were done on a Varian XL-200, although it was not evident how to quantify these data. Homonuclear correlation 2D experiments and J-coupled 2D experiments were also run on the Varian XL-200.

Registry No. **3A**, 21225-62-7; **3B**, 102340-19-2; **3C**, 102260-52-6.

The Electrochemical Reduction of Fluorenone Tosylhydrazone: Evidence Consistent with the Formation of the Tosyl Nitrene Anion Radical

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Received October 17, 1985

Fluorenone tosylhydrazone (Fl=NNHTs) undergoes one-electron reductive dehydrogenation in DMF–0.1 F $(n\text{-Bu})_4NClO_4$ to give hydrogen and its conjugate base Fl=NN^-Ts as products. Fl=NN^-Ts is subsequently reduced at more negative potential to a dianion radical (Fl=$NNTs^{\bullet 2-}$) that is stable on the cyclic voltammetric time scale. On the coulometric time scale or in the presence of added proton donors ($pK_a < \sim 29$), Fl=$NNTs^{\bullet 2-}$ decomposes to give $FlHNH_2$ and $TsNH_2$ as the principal products. A pathway is proposed for the reaction of Fl=$NNTs^{\bullet 2-}$ which involves rate-determining proton abstraction by the nitrogen atom α to the fluorene moiety. Cyclic voltammetric and chronoamperometric data are presented which are consistent with the formation of the tosyl nitrene anion radical as a short-lived, unobserved intermediate.

There is currently considerable interest in the preparation and study of hypovalent ions in the gas phase.[1,2] Hypovalent ions are defined as molecular fragments that possess less than the normal number of substituents found attached to the central atom of a typical anion or cation. For example, in the nitrogen-centered series, the nitranion (R_2N^-) is the normal anion whereas the hypovalent ions include the nitrene anion radical ($RN^{\bullet -}$), the nitrene cation radical ($RN^{\bullet +}$), and the nitrene dianion (RN^{2-}).

The goal of this work was the preparation of a hypovalent anion in the tosyl nitrene series in the condensed phase. Although there are several potential routes for the preparation of these species, the one which was chosen for study here involves the electrolytic reduction of fluorenone tosylhydrazone anion (Fl=NN^-Ts, where Fl = 9-fluorenylidene and Ts = $p\text{-}H_3CC_6H_4SO_2$) to its dianion radical. Specifically, it was hoped that the dianion radical might undergo decomposition by a pathway involving nitrogen–nitrogen bond cleavage to form either the nitrene anion radical, $TsN^{\bullet -}$, or the nitrene dianion, TsN^{2-}, as an intermediate. On the basis of product studies and the results of experiments with proton donors of varying pK_a, we conclude that the electrolytic reduction of Fl=NN^-Ts

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0022-3263/86/1951-2544$01.50/0

Table I. Coulometric Data and Product Studies for the Controlled-Potential, Electrolytic Reduction of Fl=NNHTs and FlNNTs⁻ [a]

entry	compd	conc, mM	$E_{applied}$, V	n	added cmpd [conc, mM]	product, % yield					
						Fl=NNHTs	$FlHNH_2$	$Fl{=}NNH_2$	Fl=NH	$TsNH_2$	TsH
1	Fl=NNHTs	2.46	−0.6	1.0	none	104					
2	$FlNNTs^-$	3.47	−1.4	2.5	none	44	42	3.7	4	50	5
3	$FlNNTs^-$	2.86	−1.6	2.0	none	60	41	2.6	6	37	4
4	$FlNNTs^-$	2.46	−1.6	4.0	CH_3OH [25]	27	70	2	1	75	7
5	$FlNNTs^-$	1.95	−1.6	2.0	CH_3COCH_3 [30]	60	37		1.5	45	<1
6	$FlNNTs^-$	1.44	−1.5	5.8	$(CH_3CO_2)_2CH_2$ [30]	24	62	b	13	61	6
7	$FlNNTs^-$	2.93	−1.6	2.3	CF_3COOCH_3 [60]	60				37	

[a] Electroreductions were effected at a platinum gauze electrode in DMF. Yields are based on the HPLC analyses of the electrolyzed solutions after acidification with acetic acid. $FlNNTs^-$ was prepared from Fl=NNHTs by electrolytic reduction at −0.6 V. The supporting electrolyte in the experiment in entry number 2 was 0.1 F $(CH_3)_4NPF_6$; the supporting electrolyte in the remaining experiments was 0.1 F $(n\text{-Bu})_4NClO_4$. [b] Trace.

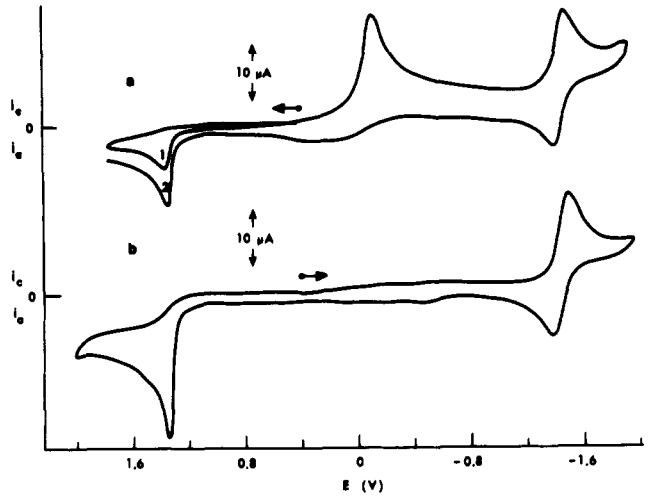

Figure 1. (a) Cyclic voltammogram of a 1.9 mM solution of Fl=NNHTs at a spherical platinum electrode in DMF–0.1 F $(n\text{-Bu})_4NClO_4$ at 22 °C. The scan was initiated at 0.4 V in the positive-going direction at a rate of 0.2 V/s; (b) Cyclic voltammogram of the exhaustively electrolyzed solution in a. The scan was initiated at 0.4 V in the negative-going direction. The numbers 1 and 2 denote the first and second cycles, respectively.

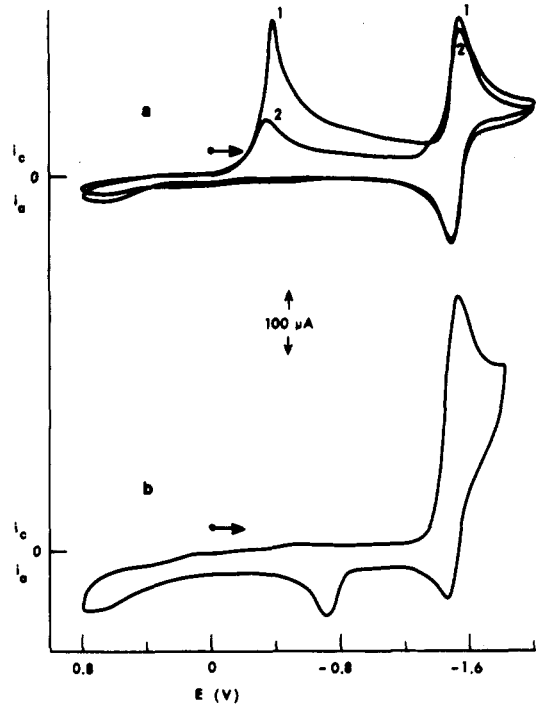

Figure 2. (a) Cyclic voltammogram for the reduction of 2.0 mM Fl=NNHTs at a planar platinum electrode in DMF–0.1 F $(n\text{-Bu})_4NClO_4$ at 22 °C. The scan was initiated at 0 V in the negative-going direction at a rate of 0.2 V/s; (b) Same as a except that 2 mM K-*t*-BuO is present.

leads mainly to nitrogen–nitrogen bond cleavage and that $TsN^{\bullet-}$ may be formed as a short-lived, unobserved intermediate.

Results

Preparation of Fl=NN⁻Ts from Fl=NNHTs. The cyclic voltammogram for the reduction of Fl=NNHTs in the absence of an added proton donor consists of an irreversible cathodic process in the vicinity of −0.2 V, an electrochemically reversible process near −1.5 V, and an irreversible anodic process at 1.36 V (Figure 1a). Single-potential-step chronoamperometry results establish that each of the reduction processes is diffusion controlled in the time range 5 ms $\leq t \leq$ 5 s and that one electron is involved in each step ($it^{1/2}/CA$ = 150 $\mu A \cdot s^{1/2} \cdot mM^{-1} \cdot cm^{-2}$ for each process; for comparison, the reversible, one-electron reduction of fluorenone azine (Fl=NN=Fl) afforded $it^{1/2}/CA$ = 148 $\mu A \cdot s^{1/2} \cdot mM^{-1} \cdot cm^{-2}$).[3] When an excess of K-*t*-BuO is added to a solution of Fl=NNHTs (Figure 2), the cathodic peak near −0.2 V disappears while the cathodic peak near −1.5 V doubles in magnitude. The product of the latter reduction is unstable in the presence of *t*-BuOH and decomposes on the cyclic voltammetric time scale to give a product that is oxidized irreversibly near −0.64 V on the reverse, positive-going sweep. Because the anodic switching potential in this particular experiment is 0.8 V, the irreversible, anodic peak that was seen in Figure 1a near 1.36 V does not appear here.

The cathodic peak at −0.2 V (Figures 1a and 2a) is attributed to the irreversible reduction of the acidic hydrogen of Fl=NNHTs to hydrogen gas. The assignment is based on the disappearance of this peak when equimolar amounts of K-*t*-BuO and Fl=NNHTs are mixed, the fact that a gas is evolved from a platinum cathode surface when Fl=NNHTs is electrolyzed in the absence of an added base at −0.6 V, and HPLC product studies. As shown by the results in entry 1 of Table I, Fl=NN⁻Ts (analyzed as Fl=NNHTs) was obtained quantitatively after Fl=NNHTs was exhaustively electrolyzed in DMF–0.1 F $(n\text{-Bu})_4NClO_4$ at the potential of the first cathodic peak ($E_{applied}$ = −0.6 V) (Figure 1b). Although the experimental n value of 1.3 exceeds the theoretical n value of 1.0 for the reduction of H^+ to hydrogen, no other nongaseous product was detected by either HPLC or cyclic voltammetry.

The reversible process near −1.5 V in Figure 2a is assigned to the one-electron reduction of Fl=NN⁻Ts to $Fl{=}NNTs^{\bullet 2-}$. $Fl{=}NNTs^{\bullet 2-}$ is stable on the cyclic voltammetric time scale in DMF–0.1 F $(n\text{-Bu})_4NClO_4$ but is

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rapidly protonated by *t*-BuOH in the presence of free K^+ (Figure 2b) or by proton donors that have pK_a's less than approximately 29 (e.g., CH_3OH, $pK_a^{Me_2SO} = 29$).[4]

The anodic peak near −0.64 V in Figure 2b is attributed to the irreversible oxidation of 9-aminofluorenyl anion ($FlNH_2^-$) to fluorenone imine (Fl=NH). The assignment is based on a comparison of this cyclic voltammetric behavior with that of authentic material under identical solution conditions[5] as well as on product studies after the controlled-potential electrolysis of Fl=NN^-Ts at −1.5 V (vide infra). The anodic peak for the oxidation of $FlNH_2^-$ is also observed in the presence of added proton donors as long as the proton donor is a weaker acid than $FlHNH_2$ ($pK_a \sim 22$).[5]

The anodic peak at 1.36 V in Figure 1 is attributed to the irreversible oxidation of Fl=NN^-Ts. This assignment is based upon the fact that it is the only anodic peak seen in the potential range from −1.3 to 2.0 V when a solution of electrogenerated Fl=NN^-Ts is scanned in the positive-going direction first. However, it should be noted that the original solution of Fl=NNHTs also usually affords an anodic peak at this potential when the cyclic voltammetric scan is initiated in the positive-going direction. The appearance of an anodic peak for the oxidation of Fl=NN^-Ts prior to its formation by electroreductive dehydrogenation of Fl=NNHTs is consistent with the presence of an adventitious basic impurity in DMF that deprotonates Fl=NNHTs rapidly and reversibly. In order to test this hypothesis, the cyclic voltammetric reduction of Fl=NNHTs was examined briefly in CH_3CN–0.1 F $(CH_3)_4NBF_4$. Under these solution conditions the anodic peak for the irreversible oxidation of Fl=NN^-Ts at 1.36 V did not appear until the electroreductive dehydrogenation of Fl=NNHTs had been effected. The anodic peak for the irreversible oxidation of Fl=NN^-Ts reappeared in CH_3CN–0.1 F $(CH_3)_4NBF_4$, however, when an equimolar amount of triethylamine was added to the solution. Although no need was felt to identify the impurity in DMF, because it had no adverse effect on the overall results, it is presumed to be dimethylamine. The slow decomposition of DMF to give dimethylamine as a product has been reported.[6]

Although either the chemical or the electrochemical method can be used to convert Fl=NNHTs into Fl=NN^-Ts, the chemical method also affords as product the conjugate acid of the base that has been added to a solution of Fl=NNHTs. In the case of K-*t*-BuO as the added base, this is undesirable because the *t*-BuOH that is formed has been seen above to protonate Fl=$NNTs^{\bullet 2-}$ in the presence of free K^+. Accordingly, all subsequent solutions of Fl=NN^-Ts were prepared by exhaustive electrolysis of Fl=NNHTs at −0.6 V.

Basicity of Fl=NN^-Ts. Several of the electroreductions of Fl=NN^-Ts in this study were performed in the presence of added proton donors. In order to demonstrate that Fl=NN^-Ts is not protonated by any of these acids in DMF, a tenfold excess of the strongest acid used in this study, CH_3COOH ($pK_a^{Me_2SO} = 11.6$),[7] was added to a solution of electrogenerated Fl=NN^-Ts. The absence of a discernible cathodic peak for the reduction of Fl=NNHTs at −0.2 V after the addition of CH_3COOH leads us to conclude that Fl=NN^-Ts is a weak base which will not be converted to its conjugate acid by any of the added proton donors used in our studies.

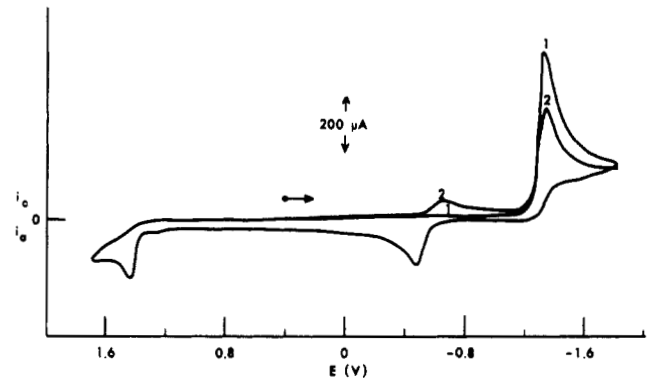

Figure 3. Cyclic voltammogram of a 2.6 mM solution of Fl=NN^-Ts at a vitreous carbon electrode in DMF–0.1 F $(n\text{-Bu})_4NClO_4$ to which 26 mM CH_3OH has been added. The temperature was 22 °C. The scan was initiated at 0.4 V in the negative-going direction at a rate of 0.2 V/s.

Products Arising from Reduction of Fl=NN^-Ts. Although Fl=$NNTs^{\bullet 2-}$ is stable ($i_{p,a}/i_{p,c} = 1.0$) on the cyclic voltammetric time scale in the absence of an added proton donor, it is too unstable to allow the recording of its ESR spectrum with the instrumentation that was available to us. Fl=$NNTs^{\bullet 2-}$ is also unstable on the coulometric time scale and undergoes decomposition in the absence (entries 2 and 3, Table I) and presence (entries 4–6, Table I) of added electroinactive proton donors to give 9-aminofluorene ($FlHNH_2$), *p*-toluenesulfonamide ($TsNH_2$), and/or the conjugate bases of these materials as the principal reduction products. Minor amounts of the nitrogen–sulfur bond cleavage products, fluorenone hydrazone (Fl=NNH_2) and *p*-toluenesulfinic acid (TsH), are also formed. Of the several electrolysis products that were detected by HPLC, Fl=NH ($E_{p,c,1} = -0.9$ V (reversible); $E_{p,c,2} = -1.7$ V (irreversible)),[5] Fl=NNH_2 ($E_{p,c} = -1.16$ V),[3,8] and $TsNH_2$ ($E_{p,c} = -1.68$ V) are electroactive at or near the potential at which Fl=NN^-Ts is reduced to Fl=$NNTs^{\bullet 2-}$.

Effects of Proton Donors on the Redox Behavior of Fl=NN^-Ts. The addition of *t*-BuOH ($pK_a^{Me_2SO} = 32.2$)[4] has no discernible effect on the stability of Fl=$NNTs^{\bullet 2-}$ in the absence of free K^+. In the presence of K^+ that is either free or ion-paired with Fl=NN^-Ts, an equimolar amount of *t*-BuOH causes the cathodic peak height for the reduction of Fl=NN^-Ts to double and an anodic peak to appear near −0.64 V for the irreversible oxidation of $FlNH_2^-$ (Figure 2b).

The weakest proton donor that affects the stability of Fl=$NNTs^{\bullet 2-}$ significantly in the absence of free alkali metal ions is CH_3OH. A tenfold excess of CH_3OH ($pK_a^{Me_2SO} = 29$)[4] causes the Fl=NN^-Ts cathodic peak to increase by a factor of three, the anodic peak for the oxidation of unreacted Fl=$NNTs^{\bullet 2-}$ to disappear, and an anodic peak for the oxidation of $FlNH_2^-$ to arise on the reverse, positive-going sweep (Figure 3). In addition, the chronoamperometric $it^{1/2}/C$ value for the reduction of Fl=NN^-Ts at −1.60 V in the presence of CH_3OH is diffusion controlled in the time range 100 ms $\leq t \leq$ 2 s and is 3.0 times larger than the corresponding value for the reduction of Fl=NN^-Ts in the absence of an added proton donor. Since the reversible reduction of Fl=NN^-Ts to

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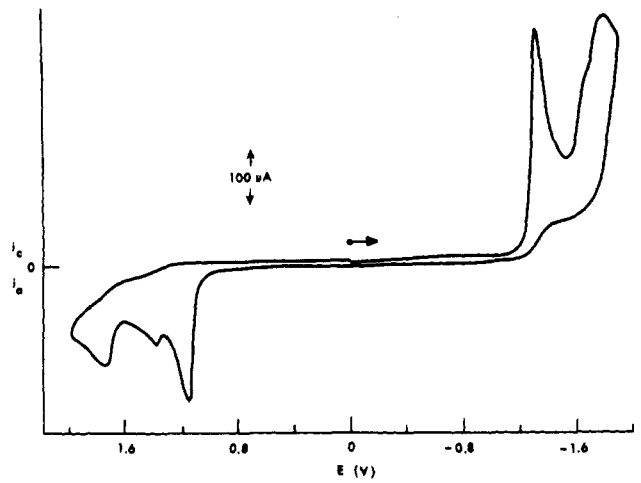

Figure 4. Cyclic voltammogram of a 1.4 mM solution of Fl=NN⁻Ts in DMF–0.1 F $(n\text{-Bu})_4NClO_4$ to which 14 mM $(EtO_2C)_2CH_2$ has been added. The working electrode was a planar vitreous carbon electrode; the temperature was 22 °C. The scan was initiated at 0 V in the negative-going direction at a rate of 0.2 V/s.

$Fl{=}NNTs^{\bullet 2-}$ in the absence of an added proton is a one-electron process, we conclude from both this and the cyclic voltammetric results that the reduction of Fl=NN⁻Ts and its decomposition products in the presence of CH_3OH corresponds to three electrons per molecule of Fl=NN⁻Ts.

Nearly identical results are obtained when CF_3CH_2OH ($pK_a \sim 22.8$)[9] is the added proton donor: the height of the cyclic voltammetric cathodic peak for the reduction of Fl=NN⁻Ts triples in magnitude, while the chronoamperometric n value is 3.0 times larger than the value that is obtained for the reduction of Fl=NN⁻Ts in the absence of the proton donor. The principal differences in the effects of CH_3OH and CF_3CH_2OH may be seen in the cyclic voltammograms. Whereas CH_3OH affords an anodic peak for the oxidation of $FlNH_2^-$ near −0.6 V, protonation of $FlNH_2^-$ by CF_3CH_2OH causes this anodic peak to disappear. However, since $FlHNH_2$ ($E_{p,c} = -1.8$ V) is reduced at significantly more negative potential than the potential at which Fl=NN⁻Ts is reduced ($E_{p,c} = -1.5$ V), protonation of $FlNH_2^-$ has no effect upon the n values that are measured by cyclic voltammetry and chronoamperometry.

The addition of an excess of $(EtO_2C)_2CH_2$ ($pK_a^{Me_2SO} = 16.4$)[10] causes the cathodic peak height for the reduction of Fl=NN⁻Ts to quadruple, the anodic peak for the oxidation of unreacted $Fl{=}NNTs^{\bullet 2-}$ to disappear, and the anodic peak for $FlNH_2^-$ ($E_{p,a} = -0.64$ V) to disappear and to be replaced by a cathodic peak for the reduction of $FlHNH_2$ ($E_{p,c} = -1.8$ V) (Figure 4). In addition, there is also a cathodic process for the reduction of $TsNH_2$ ($E_{p,c} = -1.68$ V) that appears as a shoulder on the $FlHNH_2$ peak. Anodic peaks are observed on the reverse, positive-going sweep for the oxidation of $(EtO_2C)_2CH^-$ ($E_{p,a} = 1.15$ V),[11] unreduced Fl=NN⁻Ts ($E_{p,a} = 1.36$ V) and $TsNH^-$ ($E_{p,a} = 1.7$ V) (Figure 4). With the exception of the anodic peak for Fl=NN⁻Ts, none of the anodic peaks is observed until the reduction of Fl=NN⁻Ts has been affected.

No chronoamperometric measurements of the n value can be made for the reduction of Fl=NN⁻Ts because of the proximity of the $TsNH_2$ reduction process ($E_{p,c} = -1.68$ V) to that of Fl=NN⁻Ts ($E_{applied} = -1.60$ V). It should be noted that the interference due to $TsNH_2$ was not a problem in previous chronoamperometric experiments, because none of the alcohols that were used in this study is a sufficiently strong acid to protonate $TsNH^-$.

Effect of Proton Donors on the Redox Behavior of the Fl=NN⁻Ts Reduction Products. In order to attach significance to the chronoamperometric and cyclic voltammetric n values and to identify the most plausible reaction pathways for the reduction of Fl=NN⁻Ts, the redox behavior of several of the Fl=NN⁻Ts reduction products was examined under various solution conditions. Fl=NH ($E_{p,c} = -0.9$ V), which is the expected product of the reductive cleavage of the nitrogen–nitrogen bond, is reduced reversibly to $Fl{=}NH^{\bullet -}$ on the cyclic voltammetric time scale in the absence of added proton donors. The formation of $FlNH_2^-$ as a Fl=NN⁻Ts coulometric reduction product under these conditions is believed to be the result of homogeneous redox catalysis; $Fl{=}NNTs^{\bullet 2-}$ ($E_{p,a} = -1.4$ V) and $Fl{=}NH^{\bullet -}$ ($E_{p,c} = -1.68$ V) are the proposed electrogenerated reducing agent and electron acceptor, respectively (eq 1). Endergonic electron transfer is feasible

$$Fl{=}NNTs^{\bullet 2-} + Fl{=}NH^{\bullet -} \rightleftharpoons Fl{=}NN^-Ts + Fl{=}NH^{2-} \quad (1)$$

$$Fl{=}NH^{2-} + SH \xrightarrow{\text{fast}} FlNH_2^- + S^- \quad (2)$$

because protonation of $Fl{=}NH^{2-}$ by a component (SH) of the solvent-electrolyte system is rapid and irreversible (eq 2). In the presence of CH_3OH ($pK_a^{Me_2SO} = 29$)[4] and other proton donors that will protonate $Fl{=}NH^{\bullet -}$, Fl=NH is reduced in an overall two-electron step to give either $FlHNH_2$ ($pK_a^{DMF} \sim 22$) or its conjugate base, $FlNH_2^-$.[5] $FlHNH_2$ ($E_{p,c} = -1.8$ V) is electroinactive at the potential at which Fl=NN⁻Ts is reduced ($E_{applied} \geq -1.6$ V).[5]

Certain species which would arise from nitrogen–sulfur bond cleavage in Fl=NN⁻Ts reduction are also electroactive at the applied potential. In the presence of proton donors which are sufficiently strong to effect protonation of $Fl{=}NNH^-$, $Fl{=}NNH_2$ is reduced first to Fl=NH and NH_3.[3] Fl=NH is subsequently reduced on the coulometric time scale to either $FlHNH_2$ or $FlNH_2^-$ in the manner described above.

Effect of Hydrogen Atom Donors. In order to test the possibility that $Fl{=}NNTs^{\bullet 2-}$ might react by hydrogen atom abstraction in DMF–0.1 F $(n\text{-Bu})_4NClO_4$, *N*-methylaniline ($D°(C_6H_5N(CH_3)\text{–H}) = 74$ kcal/mol)[12] and diphenylmethane ($D°(Ph_2CH\text{–H}) = 81$ kcal/mol)[13] were each added in tenfold excess as a potential hydrogen atom donor. The presence of either *N*-methylaniline or diphenylmethane had no discernible effect on the stability of $Fl{=}NNTs^{\bullet 2-}$ on the time scale of a cyclic voltammetric experiment.

Effect of Trapping Reagents for Nitrene Anion Radicals. Certain carbene and nitrene anion radicals have been shown to undergo facile carbonyl addition/radical β-fragmentation in the gas phase.[1,2,14] Attempts to trap $TsN^{\bullet -}$ with CH_3COCH_3, CF_3COOCH_3, or $(CH_3)_3CCHO$ in DMF–0.1 F $(n\text{-Bu})_4NClO_4$ were unsuccessful. In each instance, the cyclic voltammetric results were consistent with rapid reaction of the added reagent with $Fl{=}NNTs^{\bullet 2-}$. Although these reactions have not been investigated, reaction between acetone ($pK_a^{Me_2SO} = 26.5$)[15] and Fl=

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$NNTs^{\bullet 2-}$ probably involves proton transfer. The electron affinities of the remaining two compounds are sufficiently large that they are reduced at or near the potential at which Fl=NN⁻Ts is reduced. Thus, it is quite possible that $Fl{=}NNTs^{\bullet 2-}$ functions as an electrogenerated homogeneous redox catalyst for the reduction of the added reagent. In the two cases in which coulometric reduction products were examined (entries 6 and 7, Table I), no significant decrease in the $TsNH_2/FlHNH_2$ product radio was observed and no N-substituted toluenesulfonamide was detected.

Discussion

The Formation and Reduction of Fl=NN⁻Ts. The initial step in the reduction of Fl=NNHTs has been shown by chronoamperometric and product studies to involve the one-electron reductive cleavage of the nitrogen–hydrogen bond and to afford the conjugate base, Fl=NN⁻Ts, in quantitative yield (eq 3). In the absence of added proton

$$Fl{=}NNHTs + e^- \rightleftharpoons [Fl{=}NNHTs^{\bullet -}] \xrightarrow{\text{fast}} Fl{=}NN^-Ts + {}^1/_2H_2 \quad (3)$$

$$Fl{=}NN^-Ts + e^- \rightleftharpoons Fl{=}NNTs^{\bullet 2-} \quad (4)$$

$$Fl{=}NNTs^{\bullet 2-} + Ha \xrightarrow{\text{slow}} Fl^{\bullet}NHN^-Ts + A^- \quad (5)$$

(HA is an unspecified proton donor)

donors, the one-electron reduction of Fl=NN⁻Ts to $Fl{=}NNTs^{\bullet 2-}$ occurs reversibly on the cyclic voltammetric time scale near −1.5 V (eq 4). On the coulometric time scale, $Fl{=}NNTs^{\bullet 2-}$ is unstable and affords $FlNH_2^-$ and $TsNH^-$ as the principal products. In order to account for the formation of these products, cleavage of the nitrogen–nitrogen bond in $Fl{=}NNTs^{\bullet 2-}$ and the formation of multiple nitrogen–hydrogen bonds are required.

The rate-determining step in the reaction of $Fl{=}NNTs^{\bullet 2-}$ is believed to be the abstraction of a proton by the nitrogen atom adjacent to the fluorene moiety in $Fl{=}NNTs^{\bullet 2-}$ (eq 5). This suggestion is supported by the observations that (a) the addition of either *N*-methylaniline or diphenylmethane as a potential hydrogen atom donor has no discernible effect on the stability of $Fl{=}NNTs^{\bullet 2-}$, (b) proton donors, such as $(EtO_2C)_2CH_2$ and CF_3CH_2OH, markedly increase the rate of disappearance of $Fl{=}NNTs^{\bullet 2-}$, and (c) the product distribution in the absence and presence of added proton donors is the same (compare entries 2–5, Table I). Rate-determining abstraction of a proton by the nitrogen atom β to the fluorene moiety in $Fl{=}NNTs^{\bullet 2-}$ is excluded because this would regenerate $Fl{=}NNHTs^{\bullet -}$. This species has been demonstrated above to decompose by cleavage of the nitrogen–hydrogen bond to give Fl=NN⁻Ts and hydrogen (eq 3).

The Reaction of Fl•NHN⁻Ts. The product arising from the rate-determining protonation of $Fl{=}N_\alpha N_\beta Ts^{\bullet 2-}$ at N_α is presumed to be the carbon-centered radical, nitrogen-centered anion, Fl•NHN⁻Ts. This assignment of charge distribution is supported by the cyclic voltammetric anodic peak potentials for the oxidations of the fragment anions $FlNH_2^-$ ($E_{p,a}$ = −0.64 V) and $TsNH^-$ ($E_{p,a}$ = 1.7 V). This conclusion assumes that the potentials at which the radicals are reduced do not differ significantly from the potentials at which the corresponding anions are oxidized. Fl•NHN⁻Ts might then undergo reaction by one of three pathways: (a) protonation at N_β (eq 6), followed either by radical β-fragmentation of the nitrogen–nitrogen bond to give Fl=NH and TsNH• (eq 7) or by reduction and heterolytic cleavage of the nitrogen–nitrogen bond to give Fl=NH and $TsNH^-$ (eq 8); (b) one-electron to $FlNHNTs^{2-}$ (eq 9), followed either by heterolytic nitrogen–nitrogen bond cleavage to give Fl=NH and TsN^{2-} (eq 10) or by protonation, followed by heterolytic nitrogen–nitrogen bond cleavage to give Fl=NH and $TsNH^-$ (eq 11); (c) radical β-fragmentation to give Fl=NH and $TsN^{\bullet -}$ (eq 12).

Scheme I. Plausible Pathways for Fl•NHN⁻Ts Reaction

(a) Protonation at N_β

$$Fl^{\bullet}NHN^-Ts + H^+ \rightarrow Fl^{\bullet}NHNHTs \quad (6)$$

$$Fl^{\bullet}NHNHTs \rightarrow Fl{=}NH + TsNH^{\bullet} \quad (7)$$

$$Fl^{\bullet}NHNHTs + e^- \rightarrow Fl^-NHNHTs \rightarrow Fl{=}NH + TsNH^- \quad (8)$$

(b) Reduction

$$Fl^{\bullet}NHN^-Ts + e^- \rightarrow Fl^-NHN^-Ts \quad (9)$$

$$Fl^-NHN^-Ts \rightarrow Fl{=}NH + TsN^{2-} \quad (10)$$

$$Fl^-NHN^-Ts \xrightarrow{H^+} [Fl^-NHNHTs] \rightarrow Fl{=}NH + TsNH^- \quad (11)$$

(c) Radical β-Fragmentation

$$Fl^{\bullet}NHN^-Ts \rightarrow Fl{=}NH + TsN^{\bullet -} \quad (12)$$

Protonation of Fl•NHN⁻Ts, especially in the absence of added proton donors, is ruled out by the low basicity of Fl•NHN⁻Ts at the N_β site. Separate control experiments have demonstrated that $TsNH^-$, which was prepared by action of K-*t*-BuO on $TsNH_2$, does not afford a cathodic peak for the reduction of $TsNH_2$ when either CF_3CH_2OH ($pK_a \sim 22.8$)[9] or CH_3OH ($pK_a^{Me_2SO} = 29$)[4] is present as a potential proton donor.

Distinction between reduction of Fl•NHN⁻Ts (eq 9) and decomposition of Fl•NHN⁻Ts by radical β-fragmentation (eq 12) can be made on the basis of the chronoamperometric *n* value of 3 when either CH_3OH or CF_3CH_2OH is the added proton donor. It should be noted that both pathways afford Fl=NH as an electroactive intermediate; the formation of Fl=NH in the electroreduction of Fl=NN⁻Ts is evidenced by its detection in as much as 13% yield (entry 5, Table I). Thus, since one electron is consumed by the reduction of Fl=NN⁻Ts to $FlNNTs^{\bullet 2-}$ (eq 4) and another two electrons are required for the reduction of Fl=NH ($E_{p,c}$ = −0.9 V) to either $FlNH_2^-$ (in CH_3OH) or $FlHNH_2$ (in both $(EtO_2C)_2CH_2$ and CF_3CH_2OH) at the applied potential (eq 13–14), none of the remaining reac-

$$Fl{=}NH + 2e^- + H^+ \rightarrow FlNH_2^- \quad (13)$$

$$FlNH_2^- + HA \rightarrow A^- + FlHNH_2$$

(HA is $(EtO_2C)_2CH_2$ or CF_3CH_2OH, but not CH_3OH) (14)

tions can involve electron transfer when either CH_3OH or CF_3CH_2OH is the proton donor. This result clearly precludes reduction of Fl•NHN⁻Ts and *leaves radical β-fragmentation as the only reasonable reaction pathway for this species.*

If radical β-fragmentation is the predominant reaction pathway for Fl•NHN⁻Ts, $TsN^{\bullet -}$, a reaction product, must hydrogen atom abstract (eq 15) either in the absence of added proton donors or in the presence of either CH_3OH or CF_3CH_2OH and be protonated when $(EtO_2C)_2CH_2$ (eq 16) is present. Protonation of $TsN^{\bullet -}$ would afford TsNH•,

$$TN^{\bullet -} + SH \rightarrow TsNH^- + S^{\bullet}$$

(SH is a component of the solvent–electrolyte system) (15)

$$TsN^{\bullet -} + (EtO_2C)_2CH_2 \rightarrow (EtO_2C)_2CH^- + TsNH^{\bullet} \xrightarrow{e^-} TsNH^- \quad (16)$$

which would be reduced at the applied potential to $TsNH^-$ (eq 16). This last electron transfer accounts for the fourth electron that is observed when $(EtO_2C)_2CH_2$ is the added proton donor.

Although the basicity of $TsN^{\bullet -}$ is unknown, the proton affinity of $PhN^{\bullet -}$ (372 kcal/mol) is only 5 kcal/mol greater than that for $PhNH^-$.[1] If the difference in proton affinities between $TsN^{\bullet -}$ and $TsNH^-$ is similar, then, because $TsNH^-$ is not protonated by any of the alcohols used in this study, protonation of $TsN^{\bullet -}$ by the same alcohols should not be expected. On the other hand, protonation of $TsN^{\bullet -}$ by $(EtO_2C)_2CH_2$ is reasonable since this proton donor was shown to protonate $TsNH^-$ during the electroreduction of Fl=NN$^-$Ts.

Hydrogen atom abstraction from a component of the solvent–electrolyte system by $TsN^{\bullet -}$ is consistent with an overall three-electron process for the reduction of Fl=NN$^-$Ts in the presence of either CH_3OH or CF_3CH_2OH as long as the solvent-derived radical that is formed in eq 15 is electroinactive. The absence of electroactivity for the solvent-derived radical S$^{\bullet}$ is consistent with our previous finding that DMF–0.1 F $(n\text{-}Bu)_4NClO_4$ does not afford an electroactive radical when $(EtO_2C)_2C^{\bullet -}$ reacts by hydrogen atom abstraction.[11] In addition, there is not, to our knowledge, a documented example in which hydrogen atom abstraction from DMF–0.1 F R_4NX by a non-aryl radical has afforded an electroactive radical.

Although the data are most consistent with radical β-fragmentation of the nitrogen–nitrogen bond in Fl$^{\bullet}$NHN$^-$Ts and the formation of $TsN^{\bullet -}$ as an intermediate, our attempts to capture $TsN^{\bullet -}$ with CF_3COOCH_3 and CH_3COCH_3 were unsuccessful. However, since the successful capture of any carbene or nitrene anion radical phase with a carbonyl-containing compound in the condensed phase has yet to be demonstrated, the failure to obtain an N-substituted toluenesulfonamide as a product in entries 6 and 7 of Table I may merely mean $TsN^{\bullet -}$ reacts more rapidly in the condensed phase by hydrogen atom abstraction, proton abstraction, or other reaction pathways.

Formation of Nitrogen–Sulfur Cleavage Products. Studies with $p\text{-}NCC_6H_4SO_2NR_2$ (where R = H or CH_3) have shown that the one-electron reduction of $p\text{-}NCC_6H_4SO_2N(CH_3)_2^{\bullet -}$ to $p\text{-}NCC_6H_4SO_2N(CH_3)_2^{2-}$ occurs at approximately the same potential as that for the reduction of $p\text{-}NCC_6H_4SO_2NH^-$ and that $p\text{-}NCC_6H_4SO_2N(CH_3)_2^{2-}$ subsequently undergoes nitrogen–sulfur bond cleavage to give $p\text{-}NCC_6H_4SO_2^-$ and $(CH_3)_2N^-$.[16] A similar pathway (eq 17) may be occurring here for any Fl=NNHTs that escaped reductive dehydrogenation during the electrochemical preparation of Fl=NN$^-$Ts.

$$Fl{=}NNHTs + 2e^- \rightarrow [Fl^-{-}N^-NHTs] \rightarrow Ts^- + Fl{=}NNH^- \quad (17)$$

Another pathway for Ts^- formation is more likely if a proton donor has been added which can effect protonation of $TsNH^-$. $TsNH_2$, which is reduced at only slightly more negative potential ($E_{p,c}$ = −1.68 V) than that which was used for the controlled-potential electrolysis of Fl=NN$^-$Ts, has been shown to give Ts^- and NH_3 as its principal reduction products (eq 18).[17] If Ts^- were to arise because

$$2TsNH_2 + 2e^- \rightarrow Ts^- + TsNH^- + NH_3 \quad (18)$$

of inadvertent reduction of $TsNH_2$, its yield could be reduced by more judicious selection of both the electrolysis potential and the strength of the added proton donor.

Experimental Section

Instrumentation. Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporated circuits for electronic correction of ohmic potential loss between the reference and working electrodes.[18,19] Control of the potentiostat and the acquisition and processing of the rapid-scan cyclic voltammetric and chronoamperometric data were performed with a laboratory digital computer (ADAC Model 200, LSI 11/2).

Chromatography. The products of the electrolyzed solutions were separated by HPLC using a 6.35-mm diameter, 25-cm length stainless steel column packed with Alltech RP8, 10-μm mean particle size. The fluorene series of products was analyzed by using an eluting solvent of 75/25 CH_3OH/H_2O, while the tosyl series was analyzed by using a solvent composition of 40/60 CH_3OH/H_2O. All eluting solvents were buffered with 0.085 F formic acid and 0.015 F sodium formate. The flow rate was 1.0 mL/min. The HPLC system was a Beckman Model 332 with a Model 420 flow controller; fixed-wavelength detection (254 nm) was used. Standard solutions for quantitative analyses were prepared fresh daily.

Cell, Electrodes, and General Procedures. All electrochemical experiments were performed on an all-glass vacuum line. Approximately 30 mL of the solvent, DMF, was transferred by trap-to-trap distillation into an uncompartmentalized (for cyclic voltammetry and chronoamperometry) or a compartmentalized (for coulometry) electrochemical cell that had been loaded previously with the supporting electrolyte. A positive pressure of helium was maintained when the reference electrode, and compounds were transferred into the cell. Traces of oxygen, if present, were removed by several freeze–pump–thaw cycles. Helium was used to bring the cell up to atmospheric pressure.

Planar platinum and vitreous carbon working electrodes were used for most cyclic voltammetric and chronoamperometric experiments. The auxiliary electrode was a piece of platinum foil (ca. 1 cm^2) that was parallel to and approximately 1 cm away from the working electrode. All potentials listed were measured with respect to a cadmium chloride/cadmium amalgam reference electrode; the solvent in this electrode was DMF and was saturated with respect to both sodium chloride and cadmium chloride (Type A-III).[20] The potential of this electrode is −0.75 V vs. SCE. Dual reference electrodes were used in all cyclic voltammetric and chronoamperometric experiments.[21] The second reference electrode was a platinum wire which is in series with a 0.1-μF capacitor and was placed in parallel with the cadmium amalgam electrode. A glass frit separated the cadmium amalgam reference electrode from the working and auxiliary electrode compartment.

The progress of large-scale electrolysis at a large, cylindrical platinum gauze electrode was monitored periodically by cyclic voltammetry. At the conclusion of the experiment, the electrolysis mixture was protonated in a dry helium atmosphere with acetic acid. For studies involving the reduction of the conjugate base of Fl=NNHTs, Fl=NN$^-$Ts was generated in situ by exhaustive electrolysis of Fl=NNHTs at −0.6 V. Typically, complete conversion of Fl=NNHTs to Fl=NN$^-$Ts required 1.3 electrons per molecule of Fl=NNHTs, as judged by the absence of a cyclic voltammetric peak for the reduction of the starting material.

An attempt to record the esr spectrum of electrogenerated Fl=NNTs$^{\bullet 2-}$ was unsuccessful. The procedure that was used involved the electrolytic generation of Fl=NN$^-$Ts from Fl=NNHTs in the coulometry cell, the transfer of this electrolyzed solution to a quartz esr "flat" cell, and the subsequent electrochemical reduction of Fl=NN$^-$Ts to Fl=NNTs$^{\bullet 2-}$ directly within the microwave cavity. The working electrode was a small piece

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of platinum gauze that was centered in the cell window, the auxiliary electrode was a platinum wire, and the reference electrode was an aqueous SCE. In control experiments this procedure did allow the successful recording of the ESR spectra of electrogenerated nitrobenzene and fluorenone azine anion radicals.

Chemicals. Aliquots (1-L) of DMF (Burdick and Jackson) were purified by passage through a column of alumina (500 g, 80–200 mesh, Brockman activity 1, activated at 600 °C overnight) and were collected over a mixture of Davison 4-Å molecular sieves and alumina. This procedure was carried out in a dry, nitrogen-filled glovebag. After purification, the solvent was transferred immediately to the vacuum line. Acetonitrile (Burdick and Jackson) was purified according to the procedure of Walter and Ramaley, method B.[22] This procedure involves four reflux–distillation steps using, successively, anhydrous Al_2Cl_6, $KMnO_4/LiCO_3$, $KHSO_4$, and CaH_2. The purified solvent was then stored on the vacuum line over CaH_2. Fl=NNHTs was synthesized by refluxing an equimolar mixture of fluorenone and tosylhydrazine in ethanol for 30 min. After the solvent was removed, the precipitate was recrystallized twice from ethanol [mp 180–184 °C (lit. mp 180–182 °C[23]). Fluorenone hydrazone[24] and fluorenone imine[25] were synthesized according to known procedures. All other compounds were commercially available. Purities and identities of all compounds were verified electrochemically and chromatographically (HPLC) and by melting point determination, when appropriate.

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. Fl=NNHTs, 52341-51-2; $Fl{=}NNTs^{\cdot 2-}$, 102073-69-8; fluorenone, 486-25-9; tosylhydrazine, 1576-35-8.

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Dependence of ^{13}C NMR Chemical Shifts in Arylcyclopropanes on Conformation and Electron Demand

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Received June 15, 1984

The ^{13}C NMR spectra of conformationally rigid arylcylopropanes have been examined in order to determine the strength and conformational dependence of the benzene–cyclopropane interaction. Previous work with conformationally flexible arylcyclopropanes has implicated both conjugative and hyperconjugative interactions between the aromatic π-system and the bonding orbitals of cyclopropane. The substituent-induced chemical shifts are inconsistent with *either* mechanism being dominant. Replacement of the two hydrogen atoms on a cyclopropane methylene carbon with chlorine causes a reversal of the normal SCS response imposed by substitution on the aromatic ring. The model systems used were spiro[cyclopropane-1,9′-[9*H*]-fluorene], 1,1-diphenylcyclopropane, and 1,1a,6,6a-tetrahydrocycloprop[*a*]indene.

The use of ^{13}C NMR chemical shifts as a probe for changes in electron density produced by substitution has a long and checkered history.[2] The method has been most successful (as judged by the criteria of the quality of correlation between chemical shifts and σ-values,[3] calculated electron densities,[4] or chemical intuition[5]) in evaluating the chemical shifts of carbons in conjugated molecules. It is clear that in the majority of cases studied resonance structures provide an adequate model to explain the observed shifts.[6] Similar success has not been forthcoming in the analyses of aliphatic and saturated cyclic hydrocarbons.[2c,3a] It is in the fusion of a saturated hydrocarbon to a group with varying π-electron demand that the most unusual behavior of substituent-induced chemical shifts (SCS values) have been observed. Through-space, through-bond, conjugative, and hyperconjugative explanations have been invoked to explain the "normal", "inverse", and "random" behavior of SCS values in response to π-electron demand.

Our work with the conjugative properties of cyclopropane[7] required an interpretation of a number of the physical properties of the cyclopropane ring as a function of the conformation of an attached aromatic π-system. Current wisdom holds that cyclopropane is an effective π-donor,[8] utilizing one of its highest occupied, bonding orbitals (usually an e′ orbital drawn from either the Förster–Coulson–Moffitt[9] (FCM) or Walsh[10] sets). The

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