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## STRUCTURAL BIOLOGY DIVISION

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August 1995



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REACTION OF DIOXYGEN WITH A CROSS-CONJUGATED  
CARBON-CARBON DOUBLE BOND IN A  
bis-MACROCYCLIC DIIRON COMPOUND

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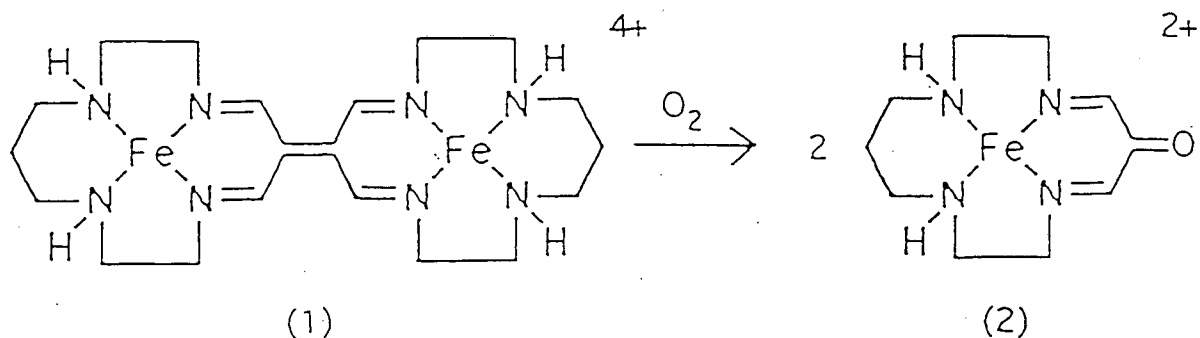
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Abstract

Atmospheric pressure dioxygen attacks a cross-conjugated carbon-carbon double bond in a diiron complex to form two, like, keto macrocyclic iron(II) complexes. This reaction occurs with high yield in both solution and in the solid state. A dioxetane intermediate is, therefore, invoked. The rate of the reaction is very dependent on the nature of the axial ligands on the low-spin iron(II) ions in the bimetallic complex. The rate is at least a factor of  $10^4$  faster with DMF ligands than with  $\text{CH}_3\text{CN}$  axial ligands. This rate dependence is explained by stabilization of a peroxo biradical transition state en route to a dioxetane intermediate. The keto-macrocyclic product has the carbonyl group conjugated with a  $\beta$ -diimine in a six-membered chelate ring.<sup>9</sup> The conformation of this keto macrocycle is fixed on the NMR time scale and all ten non-equivalent protons in the complex can be unambiguously assigned. The keto  $\beta$ -diimine ligand is an excellent  $\pi$ -acceptor as indicated by its high Fe(II) to Fe(III) oxidation potential and by the Mossbauer spectrum, which shows a low value for the center shift and a high value for the quadrupole splitting parameter.

## INTRODUCTION

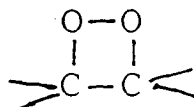
There are many different types of reactions of molecular oxygen with transition metal complexes. These include removal of electrons from the metal center or from the coordinated ligand, oxidative dehydrogenation of the ligand, and formation of metal-oxygen adducts. This paper describes a novel reaction in which a conjugated carbon-carbon double bond in a di-iron complex, **1**, reacts with dioxygen to break the double bond and form two keto-macrocylic iron complexes, **2**, shown below. This reaction occurs in high yield with atmospheric pressure dioxygen at room temperature.



We recently reported<sup>2</sup> the structure and properties of a new type of bimetallic complex that contains a cross-conjugated  $\beta$ -diimine linkage between metals in two different macrocycles, **1**. One of our first observations of this di-iron complex was that solid samples of the perchlorate salt underwent a slow reaction if exposed to the atmosphere. In acetonitrile the blue product has a  $\lambda_{max}$  at 650 nm. A similar blue product slowly formed in aerated acetonitrile solution. We have isolated and identified the blue species as the

monomer ( $\lambda_{\text{max}} = 720 \text{ nm}$ ) with DMF axial ligands is very rapidly formed in aerated DMF.

The attack of molecular oxygen on the bridging carbon-carbon double bond produces a very high percentage yield (>95%) of the keto-macrocyclic product. The high yield and the fact that the reaction also occurs in the solid state suggests that a dioxetane intermediate is involved. A mechanism for the formation of the dioxetane intermediate, which involves oxidation of one of the iron atoms, is invoked to explain the lack of similar



examples in organic systems and the very large axial ligand dependence of the rate of formation.

The proton NMR spectrum of the keto species was critical in its identification and is particularly interesting in that all ten distinct protons of the macrocycle can be unambiguously assigned. The Mossbauer spectrum of the compound is also reported and is compared to other low-spin iron-II tetraaza macrocycles. The solvent dependence of the optical spectrum, its electrochemical behavior, and the rate of formation are discussed.

### EXPERIMENTAL SECTION

All solvents used were reagent grade (99+ %) and dried over activated molecular sieves (3A) except acetonitrile which was purchased from Burdick & Jackson and used directly. In the electrochemical measurements  $\text{CH}_3\text{CN}$  was distilled from calcium hydride prior to use. All reagents were the highest quality commercially available and used without purification. Instruments used were as follows: FTIR, Nicolet 5DX; NMR, Varian Gemini 300 broadband system; UV/Vis/NIR Perkin-Elmer Array 3840 with 7500 professional computer or a Perkin-Elmer Lambda 9. Cyclic Voltammograms were measured under argon with an IBM EC 225<sup>2A</sup> or a PAR 175/173 system with tetrabutylammonium hexafluorophosphate as the electrolyte. Conditions: Pt disk working electrode; 0.1 M electrolyte; scan rate 200 mV/s. Electrospray mass spectra were measured

in a 50% aqueous acetonitrile solution (UC Berkeley Mass Spec Labs). Mossbauer spectra were obtained by Richard Frankel.

$[\text{Fe}_2(\text{C}_{20}\text{H}_{34}\text{N}_8)(\text{CH}_3\text{CN})_4](\text{ClO}_4)_4$ , **1**, was prepared by aerobic oxidative dehydrogenation of  $\text{Fe}(\text{C}_{10}\text{H}_{24}\text{N}_4)(\text{ClO}_4)_2$  as previously reported.<sup>3</sup> CAUTION: PERCHLORATE SALTS ARE POTENTIALLY EXPLOSIVE. AVOID SCRAPING COMPOUNDS WITH METAL SPATULAS AND DO NOT FILTER WITH SINTERED GLASS FILTERS.

**Preparation of  $[\text{Fe}(\text{C}_{10}\text{H}_{18}\text{N}_4\text{O})(\text{DMF})_2](\text{ClO}_4)_2$ .** A solution of **1** (0.50 g, 0.47 mmol) in DMF (25 ml) was stirred for about one hour open to air. After the initial brown color turned dark green an excess of ether was added. The solution was filtered and the powdery green solid washed with ether. Yield: .490 g (0.80 mmol, 85%).

**Preparation of  $[\text{Fe}(\text{C}_{10}\text{H}_{18}\text{N}_4\text{O})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$ , **2**.** The green  $[\text{Fe}(\text{C}_{10}\text{H}_{18}\text{N}_4\text{O})(\text{DMF})_2](\text{ClO}_4)_2$  (.490 g, 0.80 mmol) was dissolved in acetonitrile, filtered and then stirred for 30 min. Excess ether was added to complete precipitation of the blue powdery product. Filtration followed by ether washings gave .400 g (.73 mmol) of product. Yield: 91%.

**Preparation of  $[\text{Fe}(\text{C}_{10}\text{H}_{18}\text{N}_4\text{O})(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ .** An excess of  $\text{NH}_4\text{PF}_6$  (about 5:1) was added to a slurry of the  $[\text{Fe}(\text{C}_{10}\text{H}_{18}\text{N}_4\text{O})(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$  (0.400 g, 0.73 mmol) in acetonitrile (25 ml). After all the colored solids dissolved, the solution was filtered. The addition of a large excess of ether and cooling of the solution overnight completed the precipitation of the blue powdery product, which was obtained after filtration and ether washings. Yield: 0.38 g (0.60 mmol, 82%).

## RESULTS AND DISCUSSION

### Formation of **2**

The keto-macrocyclic species can be formed from the dinuclear compound **1** in a number of different ways. A slow reaction of molecular oxygen occurs with solid **1**. With crystalline salts of **1** ( $\text{CH}_3\text{CN}$  axial ligands) a surface film of the blue species forms over



periods of weeks. The solubility of 2 is much greater than 1 and the surface film can be removed by rapid washing with acetonitrile. If the solid is finely divided, the reaction with atmospheric oxygen proceeds more rapidly, with up to 15% conversion to 2 in one day.

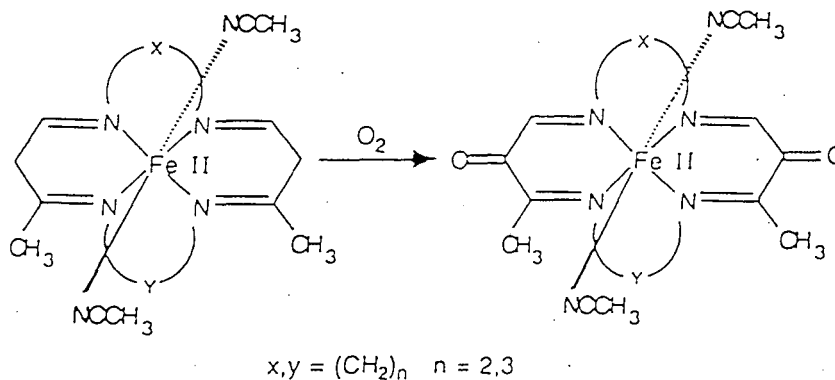
The reaction between the dinuclear compound 1 and oxygen also occurs in solution. Interestingly, the rate of this reaction is strongly solvent dependent. In oxygen-saturated acetonitrile solutions, the reaction has a half-life of over a week. In oxygen-saturated DMF the half-life for formation of 2 is less than a minute. This is greater than a factor of  $10^4$  increase in reaction rate. The reaction between the dinuclear iron compound and oxygen in DMF occurs with no appreciable build-up of intermediates as evidenced by several isosbestic points during the reaction (Figure 1). The keto compound can also be formed with other oxo-atom transfer agents such as hydrogen peroxide or hypochlorite. The reaction between the dinuclear iron compound and hydrogen peroxide in deoxygenated  $\text{CH}_3\text{CN}$  also proceeds cleanly with isosbestic points at 685 and 505 nm.

We first discuss the various data supporting the assignment of the structure of 2 with particular emphasis on the proton NMR spectrum. The Mossbauer spectrum, solvatochromism and electrochemistry are then presented followed by speculation about mechanisms of formation of the keto complex from reaction with dioxygen.

### Structure Assignment

#### UV-Visible

The optical spectrum of 2 in acetonitrile has a band at 650 nm that is too intense to be a d-d transition. In reviewing the iron macrocycle literature we noted a paper by Riley and Busch<sup>4</sup> which described the formation of a series of di-keto macrocycles by reaction



between dioxygen and  $\beta$ -diimine macrocycles. These species were all blue in acetonitrile with  $\lambda_{\text{max}}$  at 650 nm. The similarity in optical spectra suggested that a similar chromophore was present in compound **2**. Similar reactivity between dioxygen and cobalt  $\beta$ -diimine macrocycles had earlier been described by Endicott and co-workers<sup>5</sup>.

### Mass Spectrometry

The mass spectral results support the monomeric nature of **2**. The predominant observed peak in electrospray MS is at  $m/z = 365$  which corresponds to  $[\text{Fe}(\text{C}_{10}\text{H}_{18}\text{N}_4\text{O})(\text{ClO}_4)_1]^{+1}$ , ie **2** with the loss of the axial acetonitrile ligands and addition of a perchlorate counter ion.

### IR

The infrared spectrum of **2** indicates the presence of a carbonyl. The IR spectrum of the starting dinuclear compound **1** has C=N and C=C peaks of moderate intensity at 1610 and 1640  $\text{cm}^{-1}$ . The IR spectrum of **2** has a peak at 1650  $\text{cm}^{-1}$  which exhibits much greater relative intensity. This peak is in the C=O spectral region and is similar to those observed by Riley<sup>4</sup> and Endicott<sup>5</sup> in their  $\beta$ -diimine keto species.

### NMR

The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of **2** confirm its structural assignment. The proposed structure has a plane of symmetry through the carbonyl group, the iron atom, and the opposite methylene carbon atom. This plane is perpendicular to the general plane of the macrocycle and the same symmetry element is present<sup>2</sup> in the crystal structure of **1**. The keto-macrocycle has six different kinds of carbon atoms and this is observed in the  $^{13}\text{C}$  NMR spectrum. The carbonyl carbon is observed at 187.7 ppm, relative to TMS, the olefinic carbon at 176.4 ppm, and the four methylene carbon resonances range from 59.7 ppm to 33.3 ppm. It should be noted that especially long delay times of 10 seconds are necessary to detect the carbonyl carbon resonance.

Ten resonances in the  $^1\text{H}$  NMR spectrum are expected if the proposed conformation is locked on the NMR time scale. The ten resonances result from the fact that the protons at

the equatorial and axial positions of a given carbon are non-equivalent. The  $^1\text{H}$  NMR spectrum of complex **2** in acetonitrile- $d_3$  does indeed exhibit ten different resonances. Figure 2 shows the  $^1\text{H}$  spectrum of **2** and gives the numbering scheme. A summary of the assignments and coupling constants is given in Table 1. The resonances assigned to positions 8a and 8e are the most upfield and integrate to half the area of the other positions. These resonances at approximately 2.0 ppm and 1.75 ppm are partially obscured by residual, undeuterated acetonitrile and by axial ligand exchange with the deuterated solvent. These upfield multiplets are not obscured when DMSO- $d_6$  is used as the solvent. Although the multiplet patterns are not as resolved in DMSO- $d_6$ , compared to  $\text{CD}_3\text{CN}$ , the upfield multiplets still integrate to half intensity. We have used 2-D, conventional homonuclear decoupling and a limited number of NOE difference experiments to assign the observed  $^1\text{H}$  NMR resonances to specific positions in our proposed structure.

The peak at 8.77 ppm is assigned to the olefinic protons at position 2 of our model. The olefinic peak is slightly split due to a small four-bond coupling with the proton at position 4a (4.06 ppm) ( $J_{4a2} = 2.4$  Hz). The short through-space distance between these two protons has been confirmed by NOE experiments. A broad signal at 4.76 ppm is assigned to the amine protons. Amine protons typically exhibit broad NMR signals due to the quadrupole moment of the  $^{14}\text{N}$  nucleus. This signal disappears upon treatment with DCl, confirming its assignment.

The assignment of other resonances was done by determining the coupling patterns with a 2D COSY experiment (supplemental). The amine proton at 4.76 ppm was found to be coupled strongly with the resonances at 2.50 ppm and 2.78 ppm and weakly to those at 3.31 ppm and 3.53 ppm. These resonances must be due to the protons on carbons 5 and 7. The carbon 7 protons were assigned to the peaks at 2.50 ppm and 3.31 ppm because they were the only ones coupled to the half-integrated intensity upfield protons of position 8 (2.0 ppm and 1.75 ppm). The proton resonances at 4.06 ppm and 4.56 ppm were

assigned to position 4 because they were coupled to the carbon 5 protons (2.78 ppm and 3.53 ppm).

In rigid cyclic systems the equatorial proton is consistently downfield relative to the axial proton on the same carbon atom. This is the situation for **2**; however, the differences in chemical shifts of the equatorial and axial protons are larger than the usual 0.1 to 0.5 ppm range:  $\Delta(4e-4a) = 0.52$  ppm;  $\Delta(5e-5a) = 0.74$  ppm;  $\Delta(7e-7a) = 0.82$  ppm. Individual coupling constants were determined by successive decoupling experiments and measurements of resultant peak positions. The observed multiplet patterns were also reproduced by computer simulations using the experimental coupling constants.

A doublet of doublets signal at 4.56 ppm is assigned to the equatorial proton at position 4. This pattern arises from a large geminal coupling with proton 4a and a smaller vicinal coupling with proton 5a. No coupling is observed between the equatorial protons on carbon 4 and carbon 5. Our molecular mechanics models suggest that the dihedral angle between protons 4e and 5e should be very close to  $90^\circ$  where the coupling will be at a minimum.

The quasi-triplet at 4.06 ppm is assigned to proton 4a. The 1:2:1 nature of the pattern is the result of very similar coupling of 4a with protons 4c and 5a. The triplet pattern is further split by a weak vicinal coupling from the equatorial proton at carbon 5, and from the weak four-bond coupling with the olefinic proton at position 2.

The resonance consisting of two overlapping triplets centered at 3.53 ppm is assigned to proton 5e. The pattern is the result of strong geminal coupling with proton 5a and two smaller and similar vicinal couplings with proton 4a and the amine proton 6. The distorted doublet centered at 3.31 ppm (proton 7e) results from a strong geminal coupling with proton 7a together with similar vicinal couplings with proton 8e and the amine proton. The multiplet is also distorted by a weaker vicinal coupling with proton 8a.

The doubled 1:3:3:1 multiplet at 2.78 ppm is due to the axial proton on position 5. The 1:3:3:1 nature of the pattern is the result of similar large coupling constants with the

amine proton and protons 5e and 4a. The multiplet is further split by a weak vicinal coupling with proton 4e.

The multiplet at 2.50 ppm also displays a 1:3:3:1 pattern and is assigned to the 7a proton. In this case the axial proton on carbon 7 is strongly coupled to the amine proton and protons 7e and 8a. The components of the multiplet are further split by a weak vicinal coupling with proton 8e.

The upfield, partially obscured multiplets at approximately 2.0 ppm and 1.75 ppm are assigned to protons 8e and 8a respectively. The assignments are based on their one-half integrated intensity and their upfield chemical shifts.

The optical, electrospray MS, IR and particularly the  $^{13}\text{C}$  and  $^1\text{H}$  NMR taken together allow confident assignment of the structure of **2**. We now consider specific aspects of the optical, Mossbauer, and electrochemical data of **2**.

### **Physical Properties**

#### **Optical**

The absorption spectrum of complex **2** in acetonitrile (Figure 3) exhibits maxima at 650 nm ( $\epsilon = 3,660 \text{ M}^{-1} \text{ cm}^{-1}$ ), 340 nm ( $\epsilon = 2,470 \text{ M}^{-1} \text{ cm}^{-1}$ ) with a shoulder at 370 nm, and at 232 ( $\epsilon = 8,890 \text{ M}^{-1} \text{ cm}^{-1}$ ).

As mentioned earlier our initial designation of **2** as a keto-macrocyclic was based on the similarity of its optical spectrum to iron-keto  $\beta$ -diimine species previously reported by Riley and Busch<sup>4</sup>. These workers assigned the transition at 650 nm as an MLCT from iron  $d_{xz}$ ,  $d_{yz}$  orbitals to a  $\pi^*$  orbital of the ligand. We agree with this assignment for complex **2**. Solutions of **2** in different solvents have very different colors--blue in acetonitrile and olive-green ( $\lambda_{\text{max}} = 720 \text{ nm}$ ) in DMF. The change in optical spectra results from a change in axial ligands. The addition of chloride ion to an acetonitrile solution of **2** also results in a red shift ( $\lambda_{\text{max}} = 810 \text{ nm}$  with  $\text{Cl}^-$ ) of the spectral peaks (Figure 3). The simplest explanation is that the energies of metal  $d\pi$  orbitals increase as the axial ligand changes from  $\text{CH}_3\text{CN}$  to  $\text{Cl}^-$ . Thus the shifts to longer wavelengths result from bringing the metal

orbitals closer in energy to the lowest unoccupied ligand orbitals. Since all the bands shift, this might imply that all the transitions involve some type of charge transfer.

### Mossbauer

The Mossbauer spectrum of the perchlorate salt of **2** with acetonitrile axial ligands at 90 K consists of a quadrupole split doublet with a center shift of 0.36 mm/sec and a quadrupole splitting of 1.62 mm/sec. The value for the binuclear compound, **1**, is very similar<sup>3</sup>: 0.34 mm/sec and 1.63 mm/sec. The Mossbauer parameters for **2** can be compared to those for a large series of 14-membered tetraaza macrocyclic low-spin Fe(II) complexes studied by Busch and co-workers.<sup>6</sup> The literature complexes have the same 2,3,2,3 carbon linkages between the nitrogens, have axial CH<sub>3</sub>CN ligands and have perchlorate as the counter-anion so they are directly comparable. Mossbauer parameters are available for a series of such complexes ranging from the fully saturated species to those with 2, 3 and 4-carbon-nitrogen double bonds (See table in ref. 3.) The center shift value of 0.36 mm/sec is at the low range for this extensive series of closely-related complexes while the quadrupole splitting value is high. The center shift parameter is inversely related to the s electron density at the iron nucleus.<sup>7</sup> Good sigma donor and good pi-acceptor ligands both lead to increased s density and hence to lower center shift values. While  $\sigma$ - and  $\pi$ -bonding properties of ligands are additive in determining the center shift value, the quadrupole splitting is a measure of the difference between these two effects.

Busch and co-workers<sup>6</sup> concluded that  $\pi$  effects predominate in tetraazamacrocycles with carbon-nitrogen double bonds because they found a negative slope in a plot of quadrupole splitting versus center shift for their series. The low center shift and high quadrupole splitting values for **2** clearly indicate that the keto-macrocyclic ligand is an excellent  $\pi$ -acceptor. The carbonyl oxygen evidently attracts electron density and greatly increases the  $\pi$ -acid capabilities of the imine nitrogens. Only the cross-conjugated binucleating ligand of **1** has similar Mossbauer parameters and this binucleating ligand has also been identified<sup>3</sup> as an excellent  $\pi$ -acceptor ligand.

## Electrochemistry

The CV of **2** in CH<sub>3</sub>CN shows an irreversible oxidation at 930 mV vs. Fc/Fc<sup>+</sup> (Figure 4a). This is a very positive potential for oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. The stabilization of Fe<sup>2+</sup> by the keto β-diimine ligand is due to its exceptional π-acceptor properties and the greater π-donor strength of iron in the +2 oxidation state relative to the +3 level. There is a reversible one-electron reduction in CH<sub>3</sub>CN at -980 mV. This reduction may correspond to putting an electron in the keto β-diimine moiety of the ligand. There is also a second broad, poorly defined reduction wave at -1360 mV. The broad and irreversible nature of this wave is not well understood but may be due to a process corresponding to pinacol reduction with the protons coming from adventitious water.

The optical spectrum of **2** in CH<sub>3</sub>CN shows a pronounced red shift when chloride ion is added or when **2** is dissolved in DMF. The visible band is assigned as an MLCT and the spectral shifts are assumed to be due to changes in the energies of the metal orbitals as Cl<sup>-</sup> or DMF replace CH<sub>3</sub>CN as the axial ligands. If these assumptions are true, the electrochemical behavior should also exhibit an axial ligand dependence.

The electrochemistry does indeed show a marked shift with a 660 mV lower oxidation potential when Cl<sup>-</sup> is added (Figure 4b). Also, the oxidation wave with added Cl<sup>-</sup> is more reversible but this may just reflect the lower oxidation potential and hence lower reactivity of iron in the +3 oxidation state with Cl<sup>-</sup> axial ligands.

There is also an electrostatic factor to be considered. The keto Fe(II) macrocyclic species has a +2 charge when the axial ligands are CH<sub>3</sub>CN but is neutral with Cl<sup>-</sup> axial ligands. Everything else being equal, it will be easier to remove an electron from a neutral species than from one with a +2 overall charge. However, there is a similar large shift (690 mV) to a less positive oxidation potential when the axial ligands are DMF (Figure 4c). The complexes with DMF and with CH<sub>3</sub>CN axial ligands both have a +2 overall charge so we infer that the electrostatic effect is not the main reason for the shift in oxidation potential when Cl<sup>-</sup> replaces CH<sub>3</sub>CN as the axial ligands. There remains some ambiguity in

comparison of oxidation potentials of species with DMF and with CH<sub>3</sub>CN axial ligands due to the change in solvent although the ferrocinium/ferrocene reference scale minimizes such solvent effects.

### MECHANISM OF FORMATION

The mechanism for formation of the keto  $\beta$ -diimine monomer **2** from reaction of dioxygen with the cross-conjugated binuclear species **1** is not certain, but the fact that the reaction takes place with high yields in both solution and in the solid state strongly suggests that a dioxetane intermediate is formed. Dioxetane species are known to produce high yields of ketone compounds<sup>8</sup>.

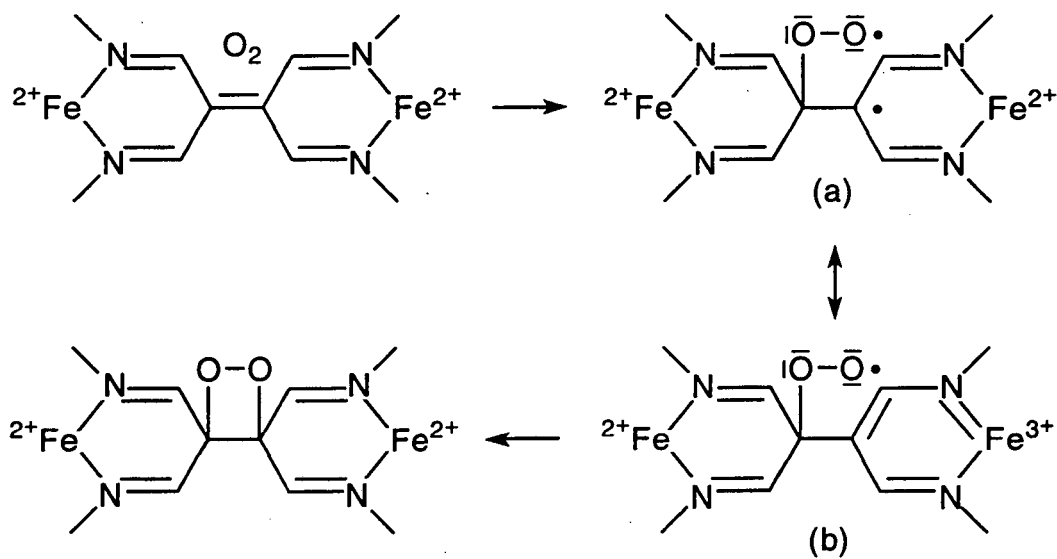
There are many examples of dioxetane intermediates formed from concerted reactions of oxygen with olefins in organic systems, but these require singlet oxygen usually produced photochemically. Presence or absence of light does not affect the reaction rate of **1** to **2**. The formation of a hydroperoxide species (ROOH) that subsequently yields the dioxetane intermediate would remove the necessity of invoking singlet oxygen. However, formation of a hydroperoxide intermediate requires the presence of an allylic hydrogen atom which is absent in the cross-conjugated ligand in **1**.

From the paucity of similar examples from the organic literature of facile room-temperature atmospheric-pressure attack of dioxygen on conjugated olefins, it appears that the iron centers in **1** are important and are directly involved. A plausible stepwise mechanism for dioxetane formation is shown in Scheme 1. The first step proceeds via transfer of one electron from the  $\pi$ -system to a dioxygen molecule. This produces a peroxide radical with concomitant formation of another radical in a six-membered chelate ring (species **a**). The total spin is conserved in this step. The proposed mechanism then involves triplet-to-singlet intersystem conversion followed by combination of the intramolecular radical pair to form the dioxetane intermediate.

A resonance form of species **a** has a quasi-aromatic arrangement with oxidation of low-spin iron II to low-spin iron III. Another way to describe this situation is that the



Scheme 1.



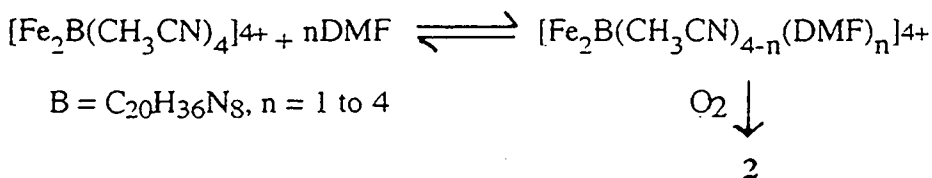
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presence of  $d_{\pi}$  electrons on the iron center stabilizes the radical in the six-membered chelate ring. Any modification of the iron center, i.e., change of axial ligands, which will favor oxidation of the iron center or promote more  $\pi$ -backbonding from the iron to the binucleating ligand, will favor formation of the dioxetane intermediate. Oxidation of **1**, presumably at the iron center, is much more difficult with axial  $\text{CH}_3\text{CN}$  ligands than with DMF. Likewise,  $\text{CH}_3\text{CN}$  molecules acting as  $\pi$ -acceptors will lower the available electron density in  $d_{\pi}$  iron orbitals. This effect may help explain the remarkable acceleration of over  $10^4$  of the rate of formation of **2** in DMF versus  $\text{CH}_3\text{CN}$ . The involvement of the iron centers may also facilitate the triplet-to-singlet intersystem conversion process.

Other explanations and mechanisms are possible but are not as likely. One possibility involves oxidation of **1** to the mixed-valence state  $(\text{Fe},\text{Fe})^{5+}$ . Dioxygen can produce the mixed-valence species in DMF but not in  $\text{CH}_3\text{CN}$ , and the accelerated rate of formation of **2** might be due to rapid reactions involving the  $(\text{Fe},\text{Fe})^{5+}$  level. The mixed-valence compound with DMF axial ligands has a  $\lambda_{\text{max}}$  at 940 nm with a large molar absorptivity coefficient ( $>15,000 \text{ M}^{-1}\text{cm}^{-1}$ ).<sup>9</sup> Therefore, it would not take a large percentage build-up of the mixed-valence form to disrupt the low intensity isosbestic point at 840 nm (Figure 1). Experiments were done in which small aliquots with about one-fourth an equivalent of dioxygen were sequentially introduced into a septum-capped cuvette containing a solution of **1** in DMF. The isosbestic points were maintained, implying that if a mixed-valence species is formed in DMF it must react extremely rapidly. However, when the mixed-valence species is produced by electrochemical oxidation of **1** in anaerobic DMF and then air is introduced a relatively slow (minutes) reaction occurs to give partial return to the original isovalent compound. This process may involve disproportionation or reaction with water since there is no evidence of formation of **2**.

Several lines of indirect evidence suggest that solvent effects are not major factors in the differences in rates in  $\text{CH}_3\text{CN}$  and DMF. The reaction to form **2** was investigated in a mixed solvent with mole fraction  $\text{CH}_3\text{CN}$  0.9, DMF 0.1. Total conversion to **2** in this

dioxygen-saturated CH<sub>3</sub>CN-rich solvent was accomplished in one hour compared to weeks in pure CH<sub>3</sub>CN. The electrochemical behavior and optical spectrum in this mixed solvent were very similar to those in pure CH<sub>3</sub>CN suggesting that CH<sub>3</sub>CN molecules were the predominant axial ligands. Our interpretation is that in the mixed solvent the reaction to form **2** proceeds by reaction of dioxygen with the small equilibrium percentage of binuclear species with DMF axial ligands.



The data do not address the interesting question of the number of DMF molecules required to activate **1** for attack by dioxygen.

Another observation points to the importance of the properties of the axial ligands and absence of major contributions by solvent effects in determining rates and paths of reactions. Addition of tetraethylammonium chloride to a DMF or CH<sub>3</sub>CN solution of **1** produces a yellow chloro species,  $[\text{Fe}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)\text{Cl}_4]^0$ . When O<sub>2</sub> is then introduced to either a CH<sub>3</sub>CN or DMF solution of the isovalent chloro species, a red mixed-valence ion  $[\text{Fe}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)\text{Cl}_4]^{+1}$  is rapidly formed in good yield (>95%). Clearly the solvent has little effect and the product of the reaction is determined by the chloride axial ligands. Subtle electronic or steric differences could explain the different products when dioxygen reacts with **1** with chloride or DMF axial ligands since there are very stringent electronic and steric requirements for formation of the four-membered dioxetane ring.

We are continuing to explore the chemistry of the iron keto β-diimine complexes, with a particular emphasis on using the keto functional group as a route to other binuclear or linked donor-acceptor complexes.

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**FIGURE CAPTIONS**

**Figure 1.** Sequential spectra taken during the reaction of dioxygen with binuclear species **1** in DMF.

**Figure 2.** Proton NMR of **2** in CD<sub>3</sub>CN. The numbering scheme is depicted in the figure. Shifts are relative to TMS.

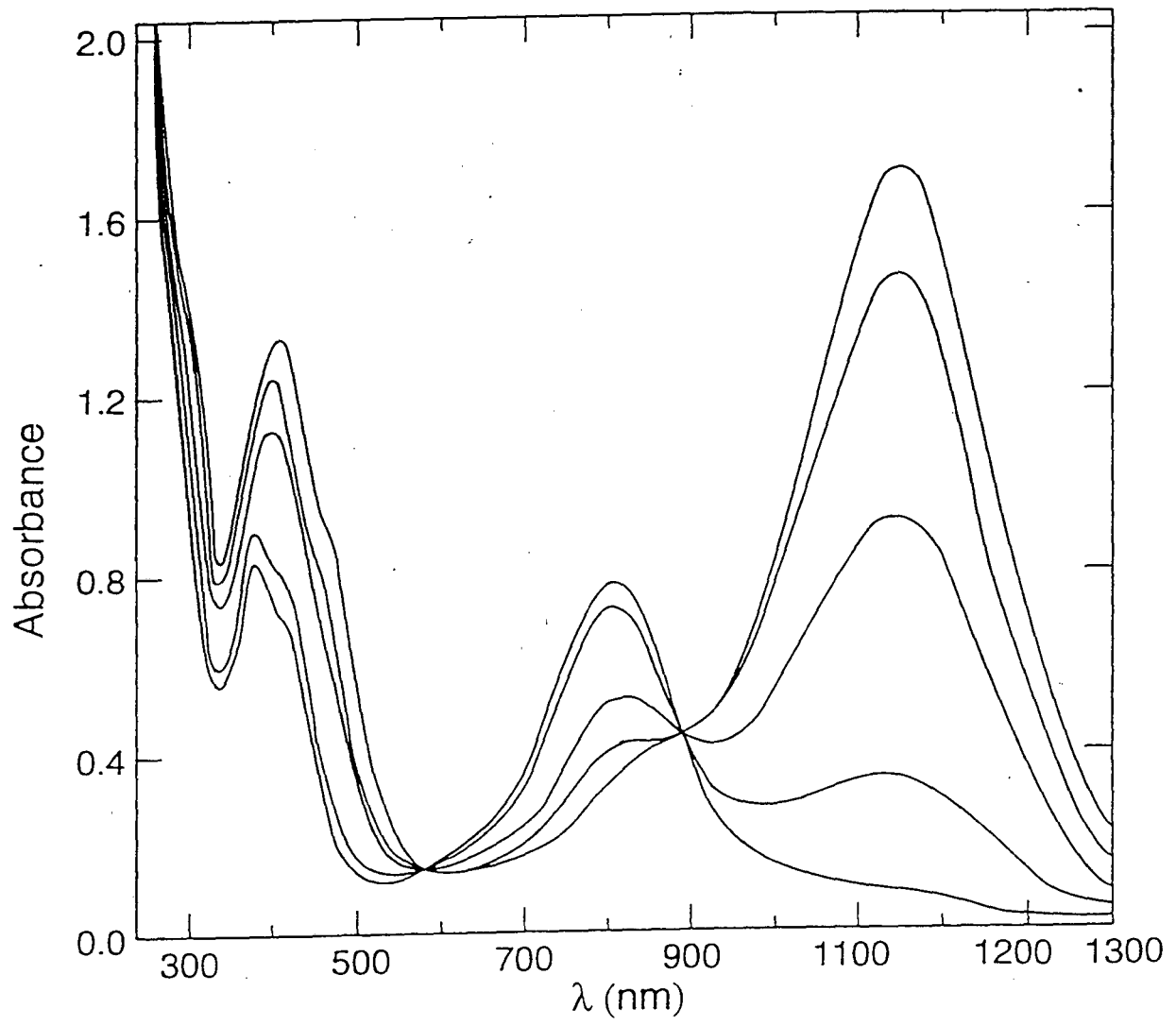
**Figure 3.** Optical spectra of **2** in CH<sub>3</sub>CN and in CH<sub>3</sub>CN with 0.05 M tetraethylammonium chloride \_\_\_\_\_.

**Figure 4.** Cyclic voltammograms of **2** in CH<sub>3</sub>CN, CH<sub>3</sub>CN with 0.1 M tetraethylammonium chloride and in DMF. Supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in CH<sub>3</sub>CN and DMF but no additional electrolyte was added to the CH<sub>3</sub>CN/Cl<sup>-</sup> solution. Conditions: Scan rate 200 mv/sec platinum working and counter electrodes, potentials measures vs. ferrocinium/ferrocene couple. A small amount of impurity of the original binuclear species **1** is observed at potentials just negative of the Fe<sup>II</sup>/Fe<sup>III</sup> oxidation.

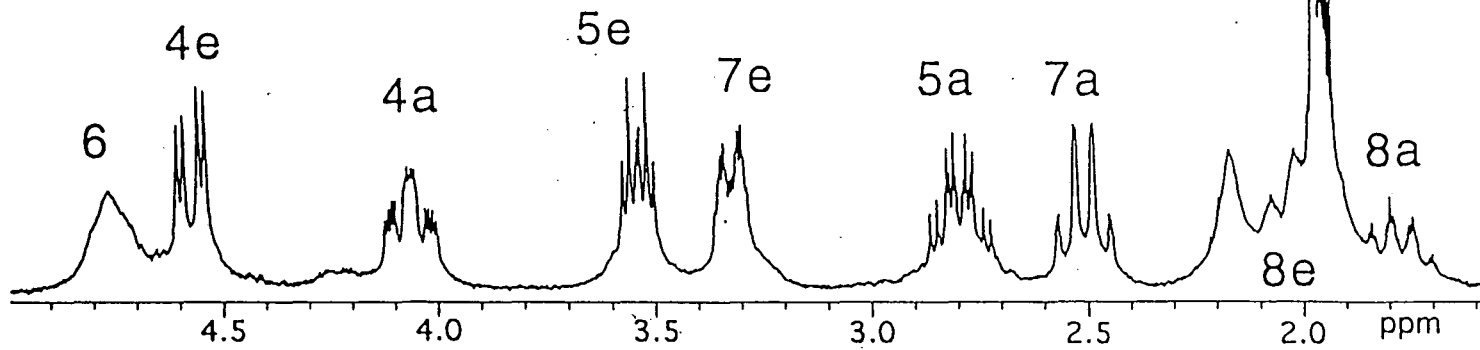
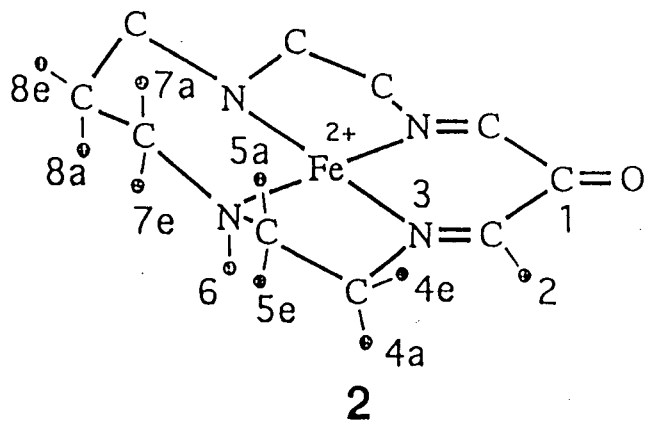
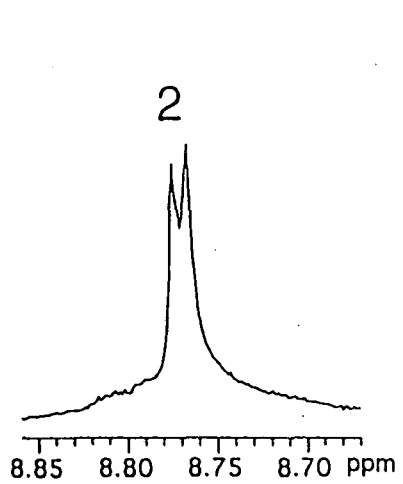
**Table 1** Proton assignments and coupling constants for 2<sup>a,b</sup>

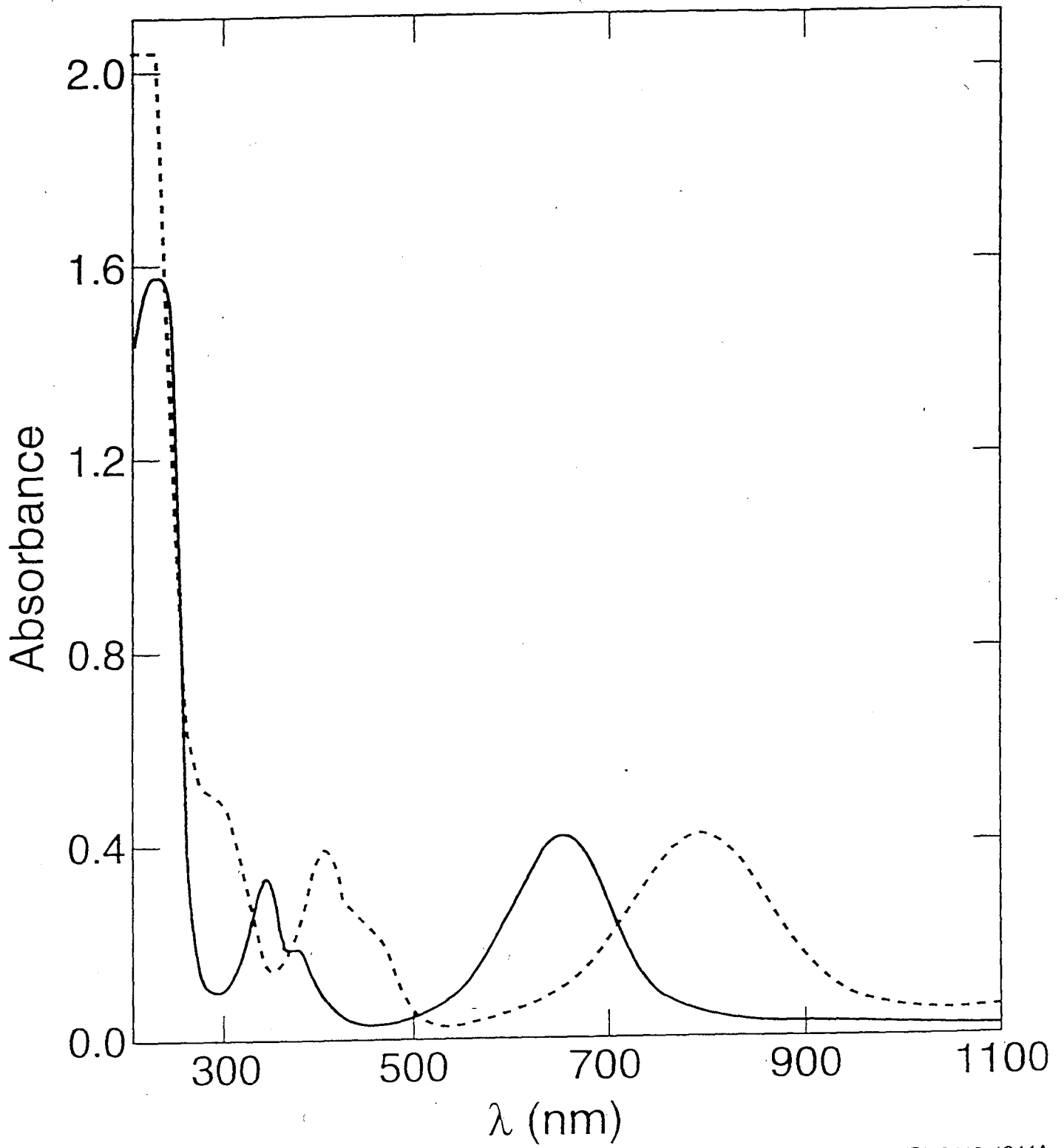
Chemical shift (ppm)	Relative integral	Assignment	Coupling Constant (Hz)
8.77	2	H 2	J <sub>4a2</sub> (2.4)
4.76	2	H 6	broad signal
4.56	2	H 4e	J <sub>4e4a</sub> (14.5), J <sub>4e5a</sub> (4.4)
4.06	2	H 4a	J <sub>4a4e</sub> (14.5), J <sub>4a5a</sub> (14.5) J <sub>4a5e</sub> (5.2), J <sub>4a2</sub> (2.4)
3.53	2	H 5e	J <sub>5e5a</sub> (11.8), J <sub>5e4a</sub> (5.2) J <sub>5e6</sub> (4.5)
3.31	2	H 7e	J <sub>7e7a</sub> (11.8), J <sub>7e6</sub> (3.8) J <sub>7e8e</sub> (3.8), J <sub>7e8a</sub> (2.4)
2.78	2	H 5a	J <sub>5a6</sub> (12.6), J <sub>5a5e</sub> (12.6) J <sub>5a4a</sub> (12.6), J <sub>5a4e</sub> (4.4)
2.50	2	H 7a	J <sub>7a6</sub> (11.8), J <sub>7a7e</sub> (11.8) J <sub>7a8a</sub> (11.8), J <sub>78e</sub> (1.7)
2.00	1	H 8c	obscured
1.75	1	H 8a	obscured

a. Coupling constants are given as absolute values. b. Chemical shifts are relative to TMS.



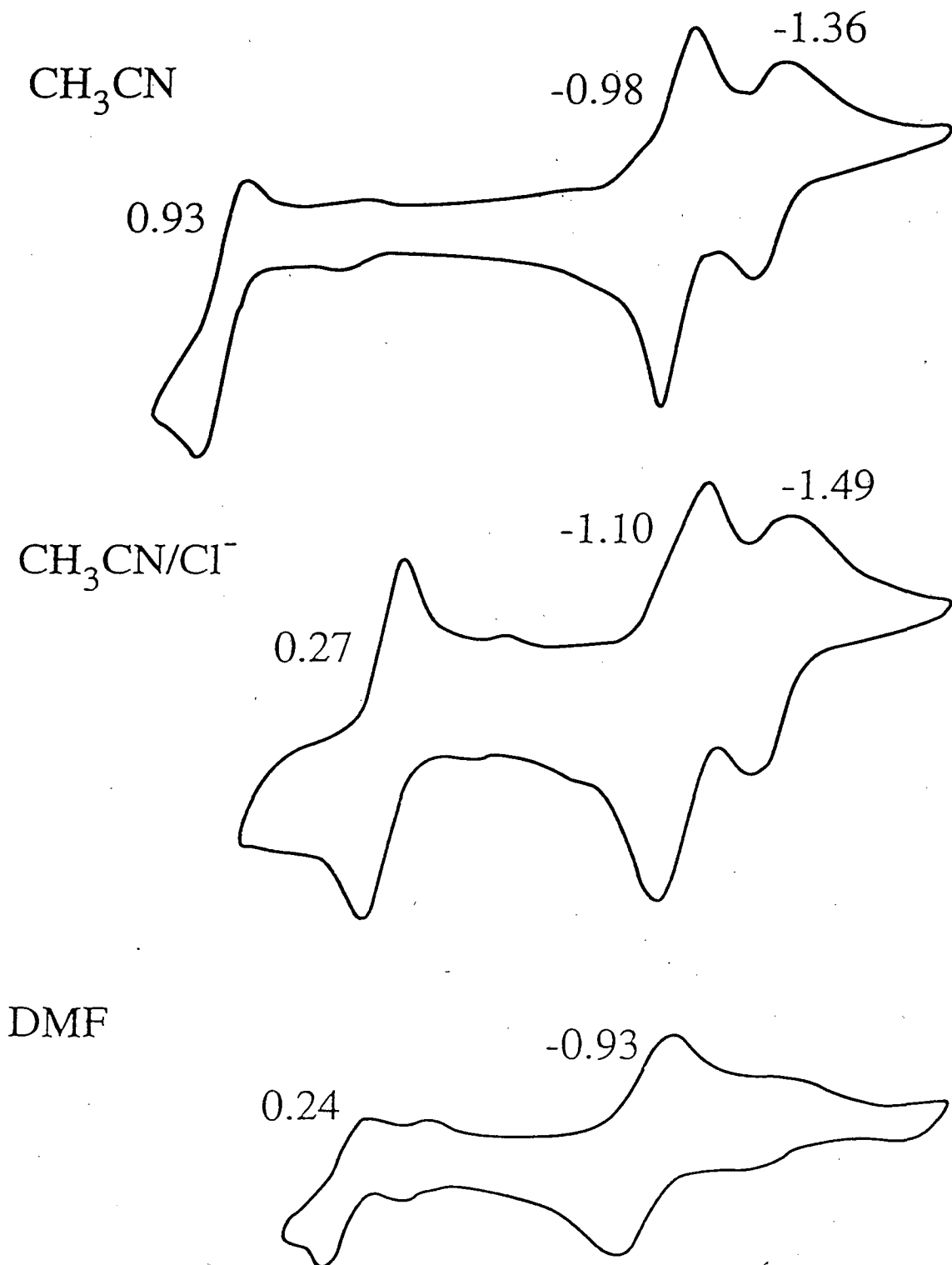






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Cyclic Voltammetry of (2)  
E vs  $\text{Fc}^+/\text{Fc}$



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