The uv–visible absorption spectra are consistent with the structural formulations of **2** and **3**.[11] In addition to the normal uv–visible absorptions, near-infrared transitions are observed at 1500 nm (ϵ 1.8 × 10^3 for **2** in acetonitrile; ϵ 1.6 × 10^3 for **3** in DMF[12]) for the mixed valence compounds **2** and **3**. A similar transition in biferrocene[Fe(II)Fe(III)] picrate **1** (1900 nm (ϵ 551)) was assigned to a photon-assisted intramolecular intervalence exchange (mixed valence transition). Based on the Hush model[2b,13,14] the energy (λ) of the mixed valence transition is dependent upon differences in geometry and bond lengths in the donor and acceptor portions of the molecule but is not very dependent upon the extent of delocalization (interaction, α) in the ground state or upon the distance separating the donor and acceptor portions of the molecule. This suggests that there is a greater geometrical change upon the partial oxidation of 1,1′-biferrocenylene than upon the partial oxidation of biferrocene. However, the intensity of the allowed transition is proportional to the probability of finding the electron on the acceptor portion in the ground state (α^2) and upon the square of the distance between the two moieties. The interaction parameter α can be approximately evaluated using the following equation[3,13]

$$\alpha^2 = \frac{4.5 \times 10^{-4}\epsilon_{\max}\Delta_{1/2}}{(\bar{\nu})(r^2)}$$

where r is the distance separating the donor and acceptor in ångströms, $\epsilon_{\max}$ is the molar absorptivity at the band maximum, $\Delta_{1/2}$ is the band half-width in wave numbers, and $\bar{\nu}$ is the frequency in wave numbers. Using the equation α^2 is calculated to be 9×10^{-3} ($\alpha = 0.095$) for biferrocene[Fe(II)Fe(III)] picrate **1**, and 4.5–5.1 × 10^{-2} (α = 0.21–0.23) for 1,1′-biferrocenylene[Fe(II)-Fe(III)] picrate or $(TCNQ)_2^-$. Based on α^2 there is about five–six times more interaction in compounds **2** and **3** than in compound **1**. The value of α for compounds **2** and **3** indicates that they are class II compounds with trapped valences ($\alpha < 0.25$).[3,15] However, it is possible that changes of phase or changes in the counterion could alter the value of α enough so that the valences would no longer be trapped.

Acknowledgments. The authors wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for grant support of this research. We acknowledge the helpful exchange of information with Dr. Ulrich Mueller-Westerhoff.

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[10] Preliminary ESCA and Mössbauer measurements indicate that the two iron atoms may be in fractional oxidation states.

[11] For compound **3** the ratio of the intensity of the 395:842 nm bands is 1.8 as observed for other $(TCNQ)_2^-$ salts: L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

[12] Spectra of DMF solutions were taken immediately after preparation, as ferricenium salts are known to decompose slowly in DMF: R. Prins, A. R. Korswafen, and A. G. T. G. Kortbeek, *J. Organometal. Chem.*, **39**, 335 (1972).

[13] N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).

[14] B. Mayoh and P. Day, *J. Amer. Chem. Soc.*, 94, 2885 (1972).

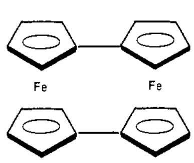
[15] When the resonance interaction (β) between the donor (i) and acceptor (j) components of the mixed valence system is as large as the thermal barrier to electron hopping (E_{th}) then complete delocalization exists. From the Hush model the thermal activation energy for electron hopping (E_{th}) is one-quarter of the activation energy for the optical electron transfer transition (E_{op}). Since the resonance interaction (β) between the i and j components is given by[14] $\beta = \alpha(E_{op})$, then α must be less than 0.25 to have trapped valences, where α is defined by the following equation.

$$\Psi_G = \sqrt{1 - \alpha^2}\phi_i + \alpha\phi_j$$

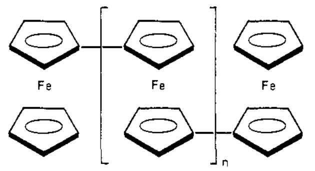
Bisfulvalenediiron and Its Iron(II–III) Mixed Valence System

Sir:

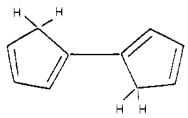
A new and convenient synthesis of [0.0]ferrocenophane (bisfulvalenediiron, "BFD") (**1**) and a description of the iron(II)–iron(III) mixed valence system derived therefrom are the subject of this communication. We were prompted to investigate the preparation of **1** *via* dihydrofulvalene **2** and fulvalene dianion **3**, because this approach, starting from simple materials and capable of being carried out without the isolation of any intermediates, seemed temptingly rational and more efficient than the two previously reported syntheses[1,2] of **1** from substituted ferrocenes.



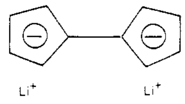
1, "BFD"



4, n = 0,1,2 . . .



2



3

Sodium cyclopentadienide (CpNa) was converted to **2** according to the procedure given by Doering and Matzner.[3] This reaction was found to proceed with approximately 70–80% conversion[4] to **2**. Subsequent addition of *n*-butyllithium afforded **3**, contaminated chiefly by cyclopentadienide.[5] Addition of ferrous chloride[6] in THF produced **1** together with polyferrocenylenes **4** (n = 0, 1, 2. . .), of which we separated only the first four.[7] BFD is known[1,2] to be only sparingly soluble in all common organic solvents, and was purified by repeated extraction (Soxhlet apparatus with

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[1] The pyrolysis of polymercuriferrocenylene affords 2–8% of BFD: M. D. Rausch, R. F. Kovar, and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **91**, 1259 (1969).

[2] F. L. Hedberg and H. Rosenberg, *ibid.*, **91**, 1258 (1969). These authors obtained **1** in unspecified yield from the Ullmann coupling reaction of 1,1′-diiodoferrocene.

[3] (a) W. v. E. Doering, "Theoretical Organic Chemistry—The Kekule Symposium," Butterworths, London, 1959; (b) E. A. Matzner, Ph.D. Thesis, Yale University, 1958.

[4] The per cent conversion to **2** was estimated from the ratio of ferrocene products.

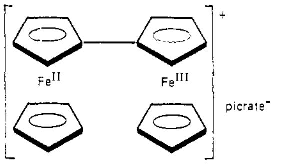
[5] The first step of this reaction presumably involves the initial formation of 5-iodocyclopentadiene, which was recently described (R. Breslow and J. M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94**, 2110 (1972)) as being surprisingly stable. We considered that the (inverse) addition of CpNa to iodine in our first reaction step might lead to a more complete conversion to **2**. However, no major change in the final product distribution was noted in this case.

[6] Used as its stable bis-THF complex: S. Herzog, K. Gustav, E. Krüger, H. Oberender, and R. Schuster, *Z. Chem.*, **3**, 428 (1963).

[7] These ferrocenes were recently described by P. V. Roling and M. D. Rausch, *J. Org. Chem.*, 37, 729 (1972).

benzene as solvent) until the nmr spectrum[8] of a sample in benzene-d_6 at 60° showed only the two triplets ($J = 2$ Hz) at τ 4.78 and 6.27 of BFD. The yield of pure **1** was 18–22%, based on starting CpNa.

The ready availablility of **1** allowed us to study the preparation of the iron(II)–iron(III) mixed valence complexes **6a–c** of this system. These compounds became particularly interesting when it was reported[9] that the related ferrocenyl–ferricinium picrate **5** possesses a broad near-infrared absorption at 1900 nm (0.65 eV), which has been associated with the electron transfer between two iron atoms in the 2+ and 3+ oxidation states.[9b,10] We were interested to see which differences would be noticeable in location and shape of a corresponding electron transfer band in the BFD mixed valence salts, in which the iron atoms are held in close proximity[11] and in a strictly rigid system.



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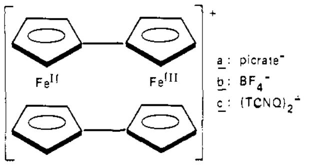

6

BFD picrate **6a** was obtained by oxidation of a benzene solution of **1** with benzoquinone in the presence of picric acid.[9] The product, after recrystallization from methanol, formed green-black needles (decomposition above 210° without melting). In a similar way, the tetrafluoroborate **6b** was prepared by benzoquinone oxidation of **1** in benzene in the presence of boron trifluoride etherate[12] and recrystallized from methanol to give green needles, which decomposed without melting above 220°. Both materials gave correct elemental analyses.

The electronic spectra of the BFD picrate **6a** and the tetrafluoroborate **6b**, which are shown in Figure 1 together with the absorption spectra of **1** and **5**, are completely identical in the long-wavelength region, where they show bands at 600 and 1500 nm. The 600-nm absorption (ϵ 370) is typical[13] in position and intensity for substituted ferricinium salts.[14] The more intense band in the near-infrared region, which we assign to an intramolecular[15] electron transfer within the cation of **6**, has its maximum intensity (ϵ 2100) at 1550 nm (0.80 eV). Closer inspection of this absorption in the frequency-linear representation (Figure 2) reveals the presence of a second transition at 1140 nm (1.09 eV) of slightly lower intensity than the 1550-nm absorption. Multiple charge transfer bands as such are well known[16] in intermolecular donor–acceptor complexes, where they may result from different ground-state configurations. The occurrence of two absorptions in the intramolecular[15] electron transfer system of **6** must be considered unusual. Of the possible reasons for the existence of two near-infrared peaks in **6**, vibrational splitting must be excluded since the peak separation ($\Delta\nu = 2300$ cm^{-1}) is too large to correspond to any infrared-active transition.[17] Without additional evidence it is impossible to assign these bands to specific transitions or to draw valid conclusions about the electronic structure of this mixed valence metallocenophane of high inherent symmetry. We are convinced, however, that the electronic spectra of **6a** and **6b** cannot be reconciled with a delocalized symmetric system with fractional oxidation states of the iron atoms. More insight into the electronic structure of **6** will come from esr, Mössbauer, and photoelectron spectroscopic data.[18]

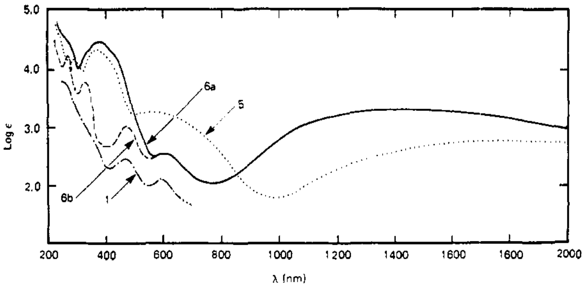

Figure 1. Electronic absorption spectra of BFD **1** in CHCl$_3$ (–·–), BFD picrate **6a** (——), BFD tetrafluoroborate **6b** (– – –), and biferrocenyl picrate **5** (···), the latter three in acetonitrile. The absorptions of **6a** and **6b** merge above 550 nm. Due to the logarithmic scale for the absorbance, the two near-infrared peaks in **6a** and **6b** cannot be distinguished.

Because of the known high conductivity of tetracyanoquinodimethane (TCNQ) radical anion salts,[19] we were interested in the properties of the BFD–TCNQ system. Steric considerations together with the knowledge that many ionic TCNQ complexes with large organic cations crystallize with formation of separate

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(8) The unsubstituted terminal cyclopentadienide ring protons of polyferrocenylenes appear as sharp singlets at higher field. This makes nmr spectroscopy the most reasonable method for assessing the purity of BFD, since most of its physical properties are unspecific with respect to polyferrocenylenes. The nmr spectrum of **1** is described in ref 2.

(9) (a) D. O. Cowan and F. Kaufman, *J. Amer. Chem. Soc.*, **92**, 219 (1970); (b) F. Kaufman and D. O. Cowan, *ibid.*, **92**, 6198 (1970).

(10) Other examples of iron(II)–iron(III) transitions in the near-infrared have been studied: G. Emschwiller and C. K. Jørgensen, *Chem. Phys. Lett.*, **5**, 561 (1970).

(11) A single-crystal X-ray diffraction study showed the iron atoms in **1** to be "symmetrically located in the center of their respective ferrocenylene moieties" at a Fe–Fe distance of 3.984 Å: M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1970 (1969).

(12) Under these conditions **4** ($n = 0$) is oxidized to the bisfluoroborate (ref 9b). In our case, only the singly oxidized salt **6b** was obtained.

(13) R. Prins, *Chem. Commun.*, 280 (1970).

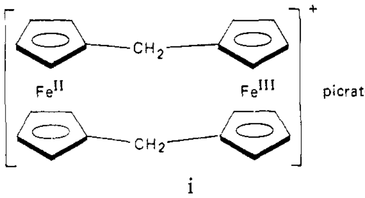
(14) The presence of a weak band at 600 nm (ϵ 130) in the spectrum of **1** is not unusual, since a similar absorption of low intensity (ϵ <50) is known (ref 13) in ferrocene.

(15) Position and molar extinction coefficient of this band in **6a** and **6b** are independent of solvent and concentration, thus making intermolecular electron transfer unlikely, and excluding external effects such as ion-pair splitting.

(16) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(17) Peaks at 680, 830, 1280, 1390, 1420, 1630, and 3100 cm^{-1} are common to the ir spectra (KBr pellets) of **6a** and **6b**.

(18) It is interesting to note at this time that [1.1]ferrocenophane (W. E. Watts, *J. Organometal. Chem.*, **10**, 191 (1967); J. T. Katz, N. Acton, and G. Martin, *J. Amer. Chem. Soc.*, **91**, 2804 (1969)) can be oxidized by the same method that led to **6a** to form the picrate **i**, which shows a strong absorption at 780 nm (1.59 eV). In this case, the two ferrocene halves are separated by sp^3 centers, but the iron–iron distance estimated from models is very close (3.9–4.6 Å, depending on conformation) to the one in BFD.



i

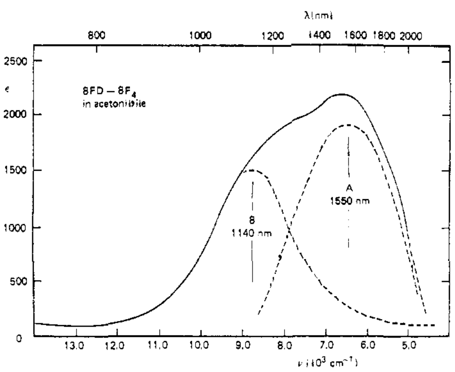


Figure 2. The near-infrared absorption of **6b** in acetonitrile (——) and its decomposition into constituent bands A and B.

columns of cations and anions[19] led us to expect the BFD–TCNQ complex to have two TCNQ units per BFD ("complex" TCNQ salt). A system of this structure should show high conductivity along the main crystal axis, since in addition to the *n*-type conduction within the TCNQ stacks there is the possibility for hole conduction in the columns of BFD cations.[20,21]

BFD was readily oxidized[22] by TCNQ in dichloromethane to give very fine green needles which, after recrystallization from absolute acetonitrile, formed flexible feltlike aggregates. Elemental analysis and electronic spectra proved this product to be the expected bis-TCNQ salt **6c** of the monooxidized BFD. The near-infrared absorption was found to be the same as in **6a** and **6b**. In addition, the absorptions of the complex TCNQ radical anion at 842 and 394 nm were observed to have the intensity found in other TCNQ salts.[23] This shows that even at very low (10^{-4} *M*) concentrations there is no equilibrium between **6c** and neutral BFD and TCNQ. Thus, the BFD–bis-TCNQ complex represents a system with both irreversible (BFD → TCNQ) and reversible (within the cation) electron transfer.

The room temperature bulk conductivity of compressed disks of **6c** was found to be consistently above $10\ \Omega^{-1}\ \text{cm}^{-1}$. This value, which represents the average over the conductivities along the crystal axes and which includes probable losses due to grain boundary effects, gives an indication that an unusually high conductivity along the main crystal axis is to be expected. We have not yet succeeded in obtaining **6c** in single crystals large enough to carry out definitive measurements to determine the magnitude, anisotropy ratios, and the mechanism of its electrical conductivity.

Acknowledgment. We wish to thank Drs. R. L. Greene and B. M. Phipps of this laboratory for the conductivity measurement and Dr. D. O. Cowan for kindly communicating to us some of his results prior to publication.

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[19] O. H. LeBlanc, Jr., "Physics and Chemistry of the Organic Solid State," Vol. 3, Interscience, New York, N. Y., p 182ff.

[20] The most recent contribution to the discussion of the conductivity mechanism in TCNQ salts is by A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, 5, 952 (1972).

[21] The BFD–bis-TCNQ system could also be viewed as a model compound for organic superconductors according to the theory by W. A. Little (*Phys. Rev. A*, 132, 1416 (1964)), inasmuch as the TCNQ columns represent the spine of such a system, while the BFD mixed valence cations correspond to the polarizable side chain of this model.

[22] Neither ferrocene nor bisferrocene **4**, $n = 0$, reacted with TCNQ under the same conditions.

[23] Y. Iida, *Bull. Chem. Soc. Jap.*, **42**, 71, 637 (1969).

[24] IBM Postdoctoral Fellow, on leave from the TH Darmstadt, Germany.

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Synthesis and Structure Determination of a Thermally Labile *anti*-Alkyl Aryl Ketoxime

Sir:

In the course of an investigation of the use of oximes of phenacyl halides as reagents for enzyme modification, it was of interest to compare the relative reactivity of the syn and anti isomers[1] of these compounds. The preparation of *anti*-α-bromoacetophenone oxime was first reported in 1901 by Korten and Scholl[2] from the reaction of α-bromoacetophenone with hydroxylamine hydrochloride in methanol. They isolated two products: *syn*-α-bromoacetophenone oxime (I), mp 97°, and a material, mp 92°, to which they assigned the anti structure, based on the belief current at that time that Beckmann rearrangements occurred by syn migration. Despite the obvious misassignment of the latter structure due to the erroneous interpretation of the Beckmann rearrangement pathway, the Korten and Scholl assignment of the stereochemistry of the 92° melting isomer remained accepted[3] until 1967 when it was proposed[4] that this material was a mixture of α-bromoacetophenone oxime and α-chloroacetophenone oxime (mp 89°) produced by halogen exchange. This proposal was later confirmed by Blumbergs, *et al.*[5] Our own mass spectrometric and nmr measurements show that the crude reaction mixture giving rise to the 92° melting material contains mainly *syn*-α-bromoacetophenone oxime and *syn*-α-chloroacetophenone oxime together with a few per cent of the anti isomers. From this mixture, only the syn isomers were isolated.

Since from the above discussion it is clear that *anti*-α-haloacetophenone oximes had not in fact been prepared previously, the synthesis of *anti*-2-bromoacetophenone oxime (II) was undertaken. The preparation of II and the X-ray determination of its structure are reported in this communication.

The reaction sequence used for the preparation of II is outlined in eq 1. Addition of 5×10^{-2} mol of I in 100 ml of CH_2CN to a solution of 0.5 mol of morpholine in 1.0 l. of H_2O at pH 9.5, followed by $CHCl_3$ extraction and crystallization ($CHCl_3$–petroleum ether), gave 3.4 $\times 10^{-2}$ mol of *anti*-α-morpholinoacetophenone oxime (III): mp 121–122° (lit.[3] mp 116–120°); nmr ($CDCl_3$) δ 7.2–7.7 (5 H, m), 3.5–3.8 (4 H, m), 3.35 (2 H, s), and 2.35–2.65 (4 H, m).[6] III (1.36×10^{-2} mol) was refluxed overnight with 6.8×10^{-2} mol of 2-methoxy-

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[1] Throughout this article, syn refers to the isomer having the alkyl group cis to the oxime oxygen; anti refers to the isomer having the akyl group trans to the oxime oxygen.

[2] H. Korten and R. Scholl, *Chem. Ber.*, **34**, 1901 (1901).

[3] H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, **45**, 2528 (1962).

[4] M. Masaki, K. Fukui, and M. Ohta, *J. Org. Chem.*, **32**, 3564 (1967).

[5] P. Blumbergs, C. B. Thanawalla, A. B. Ash, C. N. Lieske, and G. M. Steinberg, *ibid.*, **36**, 2023 (1971).

[6] This first step involves an isomerization reaction (*vide infra*).