charge-transfer states). The contribution of the ground state alone to the singlet–triplet splitting will favor the singlet in most cases, except if the overlap integral between the orbitals containing the radical electrons vanishes for symmetry reasons.[17]

The so-called McConnell mechanism has been mentioned in a quite inaccessible source[6] in a short section without being elaborated in detail. It is surprising that such a more or less spontaneous idea could give rise to such extensive experimental efforts without being checked thoroughly. Maybe our arguments will give second thoughts to experimentalists working along this line. It is already difficult enough to prepare molecules with a stable triplet ground state.[11] The additional requirement of a very small charge-transfer parameter, Δ, in order for the McConnell mechanism to work will further compound the experimental difficulties. As to the modification of the mechanism introduced by Torrance et al.,[9] it seems that it can work in principle but rests on a highly symmetrical arrangement of the molecules in the stack. It may be very difficult to achieve such an arrangement in a real system.

A word seems also in place with respect to the invokation of the McConnell mechanism for some recently discovered organometallic complexes that exhibit ferromagnetic behavior.[8,10] We do not believe that the McConnell mechanism can provide for an explanation of the ferromagnetism in any of these cases. In a subsequent paper, we will present evidence that it does not for the DMFcTCNE complex. An alternative model for the ferromagnetism of this complex will also be proposed in this paper.

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(17) Kahn, O.; Charlot, M. F. In *Valence Bond Theory and Chemical Structure*; Klein, D. J., Trinastic, N., Eds.; Elsevier: Amsterdam, 1990; p 489.

A Mechanism for the Ferromagnetic Coupling in Decamethylferrocenium Tetracyanoethenide

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Abstract: We discuss a model for the ferromagnetic coupling in a stack of alternating $[Fe(C_5Me_5)_2]^+$ and $[TCNE]^-$ ions. We present evidence against the proposed mechanism based on a model suggested by McConnell in which the ferromagnetism arises from configurational mixing of a virtual triplet excited state ($D^{2+}A^{2-}$) with the ground state D^+A^- ($D = Fe(C_5Me_5)_2$, A = TCNE). Instead, we point to a different kind of configurational mixing that involves a singly excited configuration on ferrocenium. The excitation arises from a transition between orbitals of two e_{1g} sets, which are the only ones with considerable covalent character. First, we set up the symmetry-adapted ${}^2E_{2g}$ ground- and excited-state wave functions for a single ferrocenium ion and discuss their mixing. It is shown that this mixing gives rise to an important spin correlation effect inducing negative spin densities on the Cp rings. Then the ferrocenium doublet wave functions are coupled to the TCNE doublet to form singlet and triplet wave functions for a donor–acceptor pair. The resulting singlet–triplet energy difference can be interpreted as an exchange effect between the negative spin density on the Cp rings and the radical electron density on TCNE in complete analogy to the Heitler–London model for the H_2 molecule. We obtain a term comprising a two-electron exchange integral and products of overlap and resonance integrals. Due to the negative sign of the spin density on the Cp rings, the signs of these contributions and, thus, the sign of the singlet–triplet energy splitting are inverted in our case as compared to the Heitler–London model, resulting in a triplet ground state for a donor–acceptor pair and, thus, ferromagnetic coupling. The exchange between the spin density on Fe and the one on TCNE can be neglected because the corresponding overlap densities are very small due to the large distance between Fe and TCNE (5 Å as compared to 3.5 Å for the distance Cp–TCNE). Our model corresponds to another coupling mechanism suggested by McConnell, which has nothing to do with the configurational mixing of donor–acceptor charge-transfer states.

1. Introduction

Molecular ferromagnets, both organic and organometallic, have aroused a lot of interest in recent times.[1] This is due to the ease of synthesis of organic materials. It is expected that the magnetic properties of these compounds can be tuned over a wide range by simple manipulations of the organic constituents. This would make these materials interesting for future technical applications, particularly in magnetooptics.

Different strategies, both theoretically and synthetically, have been pursued for the design of these materials. One of them is based on high-spin organic molecules, e.g., polycarbenes. Tetracarbenes with a nonet ground state[2] and pentacarbenes with $S = 5$[3] have been synthesized, but no real polymeric material of this kind is known as yet. Theoretically, many one- and two-dimensional hypothetical organic polymers with a conjugated π system and ferromagnetic coupling of their radical electrons have been suggested.[4] The ferromagnetism of these molecules results from the topology of their π electron networks in accordance with the Coulson–Rushbrooke theorem.[5] Even if these polymers with intramolecular ferromagnetic coupling could be synthesized, an intermolecular coupling mechanism would be needed in order to achieve bulk ferromagnetism. It is indeed well established that there is no one- or two-dimensional magnetic ordering.[6] Such an intermolecular coupling mechanism for conjugated π radicals has been suggested by McConnell.[7] This mechanism is based

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(1) Proceedings of the Symposium on Ferromagnetic and High Spin Molecular Based Materials. *Mol. Cryst. Liq. Cryst.* **1989**, 176.

(2) (a) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. (b) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1986**, *108*, 2147.

(3) Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1990**, *112*, 4074.

(4) (a) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372. (b) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. (c) Tyutyulkov, N.; Schuster, P.; Polansky, O. E. *Theor. Chim. Acta* **1983**, *63*, 291. (d) Tyutyulkov, N.; Polansky, O. E.; Schuster, P.; Karabunarliev, S.; Ivanov, C. I. *Theor. Chim. Acta* **1985**, *67*, 211.

(5) Coulson, C. A.; Rushbrooke, G. S. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 193.

(6) Carlin, R. L. *Magnetochemistry*; Springer Verlag: Berlin, 1986.

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Chart I

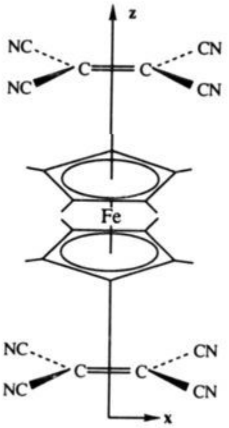
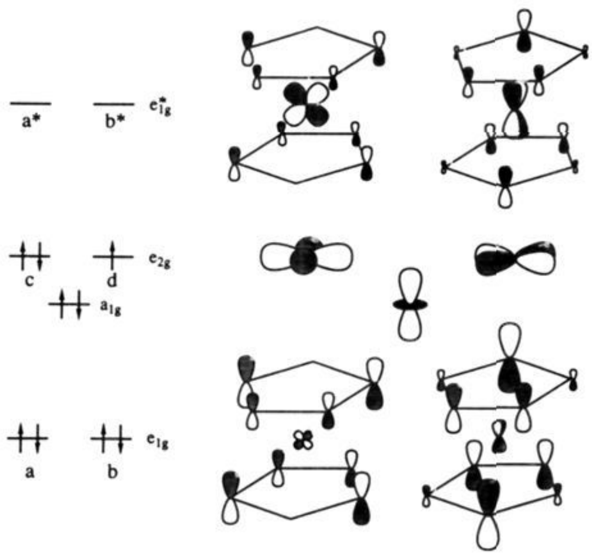


Chart II



on spin polarization leading to alternating positive and negative spin densities on the carbon backbone of these molecules.

A theoretical model also arising from the topology of conjugated polymers has been presented by Fukutome et al.[8] They propose a "polaronic" ferromagnet whose ferromagnetism is achieved by the coupling of polarons on different chain segments separated by spacers.

Another appealing strategy is that of the strict orthogonality of the magnetic orbitals. Several ferromagnetically coupled molecular species have been designed, in which the stabilization of the state of highest spin is due to this kind of orthogonality.[9] This approach has been used recently in order to obtain bimetallic molecular compounds exhibiting ferromagnetic behavior.[10]

A different approach to molecular materials exhibiting a spontaneous magnetization has been presented by one of us.[11] Bimetallic units with different spins on the two metal atoms are used as building blocks (e.g., Mn(II) or Fe(III) with $S = {}^5/_2$ and Cu(II) with $S = {}^1/_2$). Within these units, we have an antiparallel alignment of the spins, but the coupling between different units is ferromagnetic so that we have a ferrimagnet altogether.

Another mechanism supposedly leading to ferromagnetic coupling has been suggested by McConnell[12] for charge-transfer salts with certain orbital patterns. Extensive experimental efforts based on this mechanism have been pursued,[13] so far to no avail. It has been pointed out recently[14] that this mechanism is not of the general validity assumed so far and that its application is restricted to conditions that might be difficult to meet for real systems.

Several charge-transfer salts exhibiting ferromagnetic behavior have been reported recently.[15,16] The first of these was a decamethylferrocenium tetracyanoethenide $[Fe(C_5Me_5)_2]^+[TCNE]^-$ complex synthesized by Miller.[15] In the following, we will use the abbreviation DMFc$^+$ for decamethylferrocenium. The DMFc$^+$ and TCNE$^-$ ions are arranged in stacks of alternating donors and acceptors, with $D^+ = DMFc^+$ and $A^- = TCNE^-$. The molecular arrangement along the stack axis for one ferrocenium molecule and its two TCNE nearest neighbors is shown schematically in Chart I. The Cp rings in DMFc are staggered so that this molecule is of D_{5d} symmetry. In Chart I, the geometry is idealized in several respects. First of all it should be noted that the magnetic measurements of Miller have been performed for the desolvated crystal with disordered TCNE$^-$ anions so that their exact positions are not known. A complete structural determination was possible only for the solvated crystal. Nevertheless, the structural data available for the desolvated phase coincide quite well with those of the solvated phase. In the solvated crystal, we have a displacement of Fe and the central C–C bond of TCNE with respect to the stack axis (*z* axis in Chart I). Contrary to the simplified geometry shown in Chart I, which has C_s symmetry, there is no symmetry at all for a donor–acceptor pair in the solvated phase. The molecular planes of TCNE and the Cp rings are not rigorously parallel; there is a slight tilt of about 3°.

The molecular arrangement of alternating DMFc donors and TCNE acceptors in a stack provides us with one prerequisite for the application of the McConnell mechanism. It also seems that the orbital pattern for a donor–acceptor pair fits one of the configurations suggested by McConnell. Indeed, Miller himself invokes the McConnell mechanism in order to explain the ferromagnetic behavior of the complex. A critical discussion of the role of charge-transfer processes for the ferromagnetic coupling in this compound has been presented by Soos.[17] A different model based on McConnell's spin polarization mechanism[7] has been suggested by Buchachenko.[18]

We will present strong evidence that the McConnell charge-transfer mechanism cannot provide an explanation for the ferromagnetism of DMFc$^+$TCNE$^-$. Consequently, an alternative model for ferromagnetic coupling in this complex will be presented that essentially corresponds to the one suggested by Buchachenko.[18]

2. Orbital Pattern for Ferrocene and the McConnell Mechanism

Let us take a look at the orbital configuration and the shape of the frontier orbitals of ferrocene (Chart II). Such orbitals are obtained most easily by using the extended Hückel method.[19] The energetic sequence of these orbitals has been subject to some discussion. It is, e.g., an open question if the HOMO is of a_{1g}

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(7) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910.

(8) Fukutome, H.; Takahashi, A.; Ozaki, M. *Chem. Phys. Lett.* **1987**, *133*, 34.

(9) (a) Kahn, O.; Pei, Y.; Journaux, Y. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 429. (b) de Loth, P.; Karafiloglou, P.; Daudey, J. P.; Kahn, O. *J. Am. Chem. Soc.* **1988**, *110*, 5676.

(10) (a) Zhong, Z. J.; Matsumoto, N.; Okawa, H.; Kida, S. *Chem. Lett.* **1990**, 87. (b) Matsumoto, N.; Sakamoto, M.; Tamaki, H.; Okawa, H.; Kida, S. *Chem. Lett.* **1990**, 853.

(11) (a) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834. (b) Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782.

(12) McConnell, H. M. *Proc. R.A. Welch Found. Chem. Res.* **1967**, *11*, 144.

(13) (a) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927. (b) LePage, T.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 6412.

(14) Kollmar, C.; Kahn, O. *J. Am. Chem. Soc.*, preceding paper in this issue.

(15) (a) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (b) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769. (c) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* **1988**, *240*, 40.

(16) (a) Broderick, W. E.; Thompson, J. A.; Godfrey, M. R.; Sabat, M.; Hoffman, B. M.; Day, E. P. *J. Am. Chem. Soc.* **1989**, *111*, 7656. (b) Broderick, W. E.; Thomson, J. A.; Day, E. P.; Hoffman, B. M. *Science* **1990**, *249*, 401. (c) Miller, J. S.; O'Hare, D. M.; Chakraborty, A.; Epstein, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 7853.

(17) Soos, Z. G.; McWilliams, P. C. M. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 369.

(18) Buchachenko, A. L. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 307.

(19) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

or e_{2g} symmetry. Nevertheless, different ab initio calculations at the SCF level[20] agree on a ground state of $^2E_{2g}$ symmetry for the ferrocenium ion in accordance with the orbital occupation shown in Chart II, even if the HOMO is not of e_{2g} symmetry. Within the Hartree–Fock approximation, the ground state of the ion is not always obtained by removing an electron from the HOMO of the neutral molecule. In any case, the a_{1g} and e_{2g} orbitals are very close in energy. EPR data are also in line with a $^2E_{2g}$ ground state.[21] According to the coordinate system of Chart I, the e_{2g} and a_{1g} orbitals correspond to the d_{xy}, $d_{x^2-y^2}$ and d_{z^2} orbitals of Fe, respectively. These orbitals have only negligible contributions from the Cp rings; they are of almost pure metal character.[20] The e_{1g} orbitals, on the other hand, are mainly Cp orbitals, whereas the unoccupied $e_{1g}{}^*$ orbitals are dominated by the d_{xz} and d_{yz} orbitals of Fe with some rather large contributions from the Cp rings. It should therefore be noted that the MO configuration of the metal d orbitals resembles that of a transition metal in an octahedral environment. There are three metal orbitals (e_{2g} and a_{1g}) below two metal–ligand antibonding orbitals ($e_{1g}{}^*$). We have assigned convenient labels to those frontier orbitals that we will need frequently in the following (a, b, c, d, a*, b* in Chart II).

Of course, the orbitals for ferrocene and ferrocenium cannot be expected to be exactly the same. Some orbital reorganization is inevitable when we remove an electron from a molecule. This orbital reorganization is especially strong in the case of ferrocene.[20] Thus, Koopman's theorem for the calculation of the ionization energy does not apply. Although the results of the two ab initio Hartree–Fock calculations mentioned above[20] differ in several respects, they both agree that it is mainly the e_{1g} orbitals a,b and a*,b* which are strongly affected by ionization. These orbitals are the only ones with contributions from both the metal and the Cp rings and, thus, some covalent character between Fe and the Cp rings. All the other orbitals are strongly dominated by either the metal or the Cp rings. It turns out that this covalent character is strongly enhanced for the ferrocenium ion. This is reflected in the charge distribution of the molecule. Although ionization means removal of an electron from an e_{2g} and, thus, a metal orbital, the charge on Fe remains almost constant on ionization. Instead, it seems as if the charge has actually been removed from the Cp rings, because the charge difference between the neutral molecule and the ion can be localized there. This is due to the orbital reorganization just mentioned; the e_{1g} orbitals a and b that had dominant Cp character for neutral ferrocene acquire a stronger contribution from Fe for the ion. The charge removal from Fe is therefore almost completely compensated by a charge shift from Cp to Fe within the occupied e_{1g} orbitals.[20]

Another important effect also affecting the covalent character of the e_{1g} and $e_{1g}{}^*$ orbitals is due to the permethylation of the Cp rings in DMFc. Actually, we have to be careful in distinguishing two effects. The first involves the direct orbital interaction and the corresponding shifts in orbital energies due to ring–methyl orbital overlap (hyperconjugation). The second is the inductive effect, i.e., the net electron density transfer from the donor (methyl) to the acceptor (Cp ring). It has been shown by a nice perturbation theory analysis[22] that this second effect is very small for a methyl group attached to a conjugated π system. Thus, the donor character of a methyl group might be almost negligible. Nevertheless, the first effect has important consequences. The interaction of methyl and Cp ring orbitals will undoubtedly increase the energy of the Cp π orbitals, shifting them closer to the Fe d orbitals. This has been confirmed experimentally by photoelectron spectroscopy for several metal-coordinated Cp rings.[23] These experiments show that there is also a slight decrease in the valence ionization potentials of Fe; i.e., an upshift of the Fe d orbital energies as has been confirmed by cyclic voltammetry experiments[24] where a negative shift of 0.53 eV of the oxidation potential of decamethylferrocene with respect to ferrocene is observed. This must be the result of an increased electron density on Fe, which in turn might be due to an increased donating capability of the Cp ring caused by the energetic upshift of its π orbitals. But the energy shift of the Fe d orbitals is smaller than the one of the Cp π orbitals so that we still end up with a narrower gap between them.[23] Thus, the mixing between the Fe and the ring orbitals of e_{1g} symmetry will be enhanced. The permethylation therefore also contributes to an increased covalent character of the e_{1g} and $e_{1g}{}^*$ orbitals. We tried to confirm these arguments by an extended Hückel calculation with the parameters given in the Appendix. Unfortunately, although the effect appears qualitatively, its magnitude is disappointingly small. The upshift of the e_{1g} orbitals in the permethylated compound DMFc with respect to ferrocenium amounts to 0.3 eV, whereas the electron charge on Fe is enhanced by only 0.01 electrons. This small amount of additional charge is certainly not enough to cause a significant shift in the oxidation potential as it has been observed in cyclic voltammetry experiments.[24] This cannot be realistic given the fact that the permethylation is necessary in order to oxidize the donor ferrocene in the presence of the acceptor TCNE. It is known from the experiments that unpermethylated ferrocene TCNE, contrary to DMFcTCNE, has no free spins and is therefore diamagnetic.[15]

The McConnell mechanism for $DMFc^+TCNE^-$ is based on a second forward charge transfer from the e_{2g} orbital to the π^* orbital of TCNE, resulting in $DMFc^{2+}$ and $TCNE^{2-}$. This leaves us with two electrons for the two e_{2g} orbitals that according to Hund's rule form a triplet. Miller et al. argued that the mixing with this charge-transfer state stabilizes the low-lying triplet of $DMFc^+TCNE^-$ more strongly than the corresponding singlet, thus providing for a triplet ground state of the donor–acceptor pair. The energy stabilizations due to charge transfer in general can be described by second-order perturbation theory terms:

$$\Delta E = \frac{|\langle \mathrm{GS}|\hat{H}|\mathrm{CT}\rangle|^2}{\Delta} \tag{1}$$

GS and CT denote the ground and charge-transfer state, respectively. Several questions arise in connection with this argument. One of them concerns the possibility of a second oxidation step, resulting in the 2-fold charged ions. Although we do not know of any data for the charge-transfer energy Δ for this second charge-transfer step, this quantity might be large, because it will cost a lot of energy to transfer a second electron from the already ionized donor to the acceptor. We have shown in a previous paper[14] that Δ must be a small quantity in order for the mechanism to work. It should not exceed the order of magnitude of the exchange integral K_{cd} between the degenerate donor orbitals c and d. Moreover, there are other charge-transfer states that have to be considered. A backward charge transfer from the π^* orbital of the acceptor to the donor will undoubtedly stabilize the singlet. Such a charge transfer might be more likely than a further forward charge transfer. But it is not only the term Δ in the denominator of eq 1 that speaks against the McConnell mechanism. Let us consider the mixing matrix element in the numerator. The magnitude of this matrix element will depend on the overlap between the orbitals involved in the charge transfer. These are the π^* orbital of TCNE and either c or d of DMFc. The latter orbitals are localized almost completely on the metal and have only minor contributions from the Cp rings. Since the distance between Fe and TCNE is as much as ~5 Å, the overlap with the π^* orbital of TCNE will be negligibly small. A possible mixing with charge-transfer states will therefore preferably involve orbitals with some contribution from the Cp rings, because the distance between TCNE and the Cp ring is ~3.5 Å, still rather large but considerably smaller than the Fe–TCNE distance.

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(20) (a) Bagus, P. S.; Walgren, U. I.; Almlof, J. *J. Chem. Phys.* **1976**, *64*, 2324. (b) Coutière, M. M.; Demuynck, J.; Veillard, A. *Theor. Chim. Acta* **1972**, *27*, 281.

(21) (a) Prins, R.; Reinders, F. J. *J. Am. Chem. Soc.* **1969**, *91*, 4929. (b) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1970**, *92*, 3233.

(22) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370.

(23) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839.

(24) Gale, R. J.; Singh, P.; Job, R. *J. Organomet. Chem.* **1980**, *199*, C44.

It should be noted that the mixing matrix elements for the forward charge transfer described above vanish completely for symmetry reasons if we refer to the idealized geometry shown in Chart I where both the ferrocenium and the TCNE molecule are centered on the z axis. For this geometry, the orbitals c and d of ferrocenium are orthogonal to the π^* orbital of TCNE.[17]

Given all these arguments, we are firmly convinced that we can rule out the McConnell mechanism as a possible explanation for the ferromagnetic behavior of DMFcTCNE and that configurational mixing with donor–acceptor charge-transfer states is not crucial for the ferromagnetic coupling in this compound. It is therefore necessary to look for an alternative model. We will present such a model in the following. It will also be based on configurational mixing but not with a donor–acceptor charge-transfer state. Instead, we will focus on the mixing of the ground state of decamethylferrocenium with a singly excited state on the same molecular unit.

3. Electronic Configuration of Ferrocenium

Ferrocenium is an open-shell system with a total spin of $S = {}^1/_2$. This causes some complications with respect to the calculation of its Hartree–Fock ground state. The difficulties arise from the different number of electrons with spin α ($m_s = +{}^1/_2$) and spin β ($m_s = -{}^1/_2$). Among the paired electrons, the half with spin α will interact with the unpaired electron of, say, spin α in a different way as compared to the half with spin β. This is due to the Pauli principle, which prohibits two electrons of the same spin from being simultaneously at the same point in space. Thus, two electrons in two different orbitals have a lower Coulomb repulsion if they are of the same spin than if they are of different spin. This phenomenon is called "exchange stabilization".[25] To put it differently, we could also say that the motion of electrons with parallel spin is already correlated in the simple Hartree–Fock picture without configuration interaction, whereas the motion of electrons with antiparallel spin is not.

Given the fact that electrons with different spins experience different interactions in an open-shell system, it is consequent to give up the notion of paired electrons and to allow for different orbitals for different spins. This is done in the "unrestricted Hartree-Fock (UHF) method",[26] which uses different Fock Hamiltonians for α and β spins, resulting in a spin polarization effect that can lead to negative spin densities in parts of the molecule. Thus, the UHF method is sometimes referred to as "spin-polarized" Hartree–Fock method. Unfortunately, the resulting wave function is no longer an eigenfunction to the spin operator $\hat{S}^2$. Since we need definite spin eigenstates, we cannot refer to this method. The most general and the most rigorous restricted Hartree–Fock method for open-shell systems (ROHF method) has been developed by Roothaan.[27]

There are two major difficulties in the restricted Hartree–Fock treatment of open-shell systems. The first has to do with symmetry and concerns also the unrestricted approach. In contrast to the closed-shell case, the Fock Hamiltonian of an open-shell system does not necessarily transform as the completely symmetric representation of the point group of the molecule. This happens when a set of degenerate orbitals belonging to the same irreducible representation is only partially occupied. As a consequence, the MO's resulting from such a Fock Hamiltonian in general only transform as irreducible representations of a subgroup but not of the full point group of the molecule.[28] Nesbet[28] avoided this difficulty by imposing symmetry and equivalence restrictions on the Fock matrix. In Roothaan's method,[27] the total energy of a molecule is expressed as the sum over all degenerate, i.e., equivalent, ground-state wave functions:

$$E = \frac{1}{g_\alpha}\sum_i \langle \Psi^{\alpha,i}|\hat{H}|\Psi^{\alpha,i}\rangle \qquad (2)$$

g_α is the dimension of the irreducible representation Γ_α of the ground state configuration. It is easily shown that eq 2 is invariant under all operations of the group. The Fock Hamiltonians derived from eq 2 transform as the completely symmetric representation. The partial occupation of the irreducible set is taken into account by a fractional occupation number f and two additional parameters a and b depending on f.[27]

A second difficulty is encountered in the derivation of the Hartree–Fock equations for the open-shell system. In contrast to the closed-shell case, not all off-diagonal Lagrangian multipliers in the Hartree–Fock equations can be removed simultaneously by a simple unitary transformation among the occupied MO's.[27] In the open-shell case, we have two subspaces, one for the closed-shell part of the MO's and the other one for the open-shell part, i.e., the partially occupied MO's. It is still possible to remove the off-diagonal Lagrangian multipliers within the closed shell and within the open shell but not those coupling orbitals of the two different shells. Thus, at first sight, it seems as if the general open-shell case cannot be reduced to an eigenvalue problem. Roothaan,[27] however, showed by introducing additional exchange coupling operators that this is still possible. Roothaan's open-shell Hamiltonian has been expressed by McWeeny[29] in a more transparent form using density matrices:

$$\hat{F} = \hat{R}_o'\hat{F}_c\hat{R}_o' + \hat{R}_c'\hat{F}_o\hat{R}_c' + \hat{R}_e'\frac{\hat{F}_c - f\hat{F}_o}{1-f}\hat{R}_e' \qquad (3)$$

$\hat{R}_c$, $\hat{R}_o$, and $\hat{R}_e$ are the density matrices of the closed, open, and empty shell, respectively. $\hat{R}_c'$, $\hat{R}_o'$, and $\hat{R}_e'$ are their complements, e.g., $\hat{R}_c' = 1 - \hat{R}_c$, or, since $\hat{R}_c + \hat{R}_o + \hat{R}_e = 1$, $\hat{R}_c' = \hat{R}_o + \hat{R}_e$. The density matrices $\hat{R}_c$, $\hat{R}_o$, and $\hat{R}_e$ can also be considered as projection operators corresponding to the three subspaces spanned by the MO's of the closed, the open, and the empty shell, respectively. For example, $\hat{R}_c$ applied to an arbitrary vector projects the component of this vector in the subspace of the closed shell. $\hat{F}_c$ and $\hat{F}_o$ are Fock operators referring to the closed and open shell, respectively.[27]

In our specific case, the closed shell consists of all doubly occupied MO's up to the a_{1g} orbital shown in Chart II. The open shell is given by the partially occupied irreducible set of e_{2g} orbitals. Since there are three electrons for four e_{2g} spin orbitals, the fractional occupation number f is ${}^3/_4$. The constants a and b occuring in the treatment of Roothaan are obtained by calculating the total energy according to eq 2 and comparing the resulting expression to the one given by Roothaan.[27] We obtain

$$a = b = {}^8\!/_9 \qquad (4)$$

Thus, we finally obtain the following Fock Hamiltonians for the closed and the open shell:

$$\hat{F}_c = \hat{h} + \sum_k(2\hat{J}_k - \hat{K}_k) + {}^3\!/_4(2\hat{J}_c - \hat{K}_c + 2\hat{J}_d - \hat{K}_d)$$
$$\hat{F}_o = \hat{h} + \sum_k(2\hat{J}_k - \hat{K}_k) + {}^2\!/_3(2\hat{J}_c - \hat{K}_c + 2\hat{J}_d - \hat{K}_d) \qquad (5)$$

The summation index k extends over all orbitals of the closed shell. The Coulomb and exchange operators $\hat{J}$ and $\hat{K}$ are defined as usual:

$$\hat{J}_c\Psi(1) = \int dv_2\, c^*(2)c(2)\frac{e^2}{r_{12}}\Psi(1)$$
$$\hat{K}_c\Psi(1) = \int dv_2\, c^*(2)\Psi(2)\frac{e^2}{r_{12}}c(1) \qquad (6)$$

Contrary to the UHF method mentioned at the beginning of this section, the spin polarization effect is lost in the restricted method just described. It is obvious that a restricted wave function with the same orbitals for α and β spins cannot lead to negative spin densities. The spin polarization effect that will turn out to be important in our case can be recovered, however, by taking

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(25) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin Inc.: New York, Amsterdam, 1966; p 70ff, 264ff.

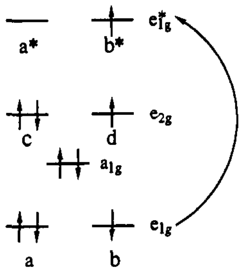
(26) (a) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571. (b) Berthier, G. *J. Chim. Phys. Phys.-Chim. Biol.* **1954**, *51*, 363.

(27) Roothaan, C. C. J. *Rev. Mod. Phys.* **1960**, *32*, 179.

(28) Nesbet, R. K. *Proc. R. Soc. London* **1955**, *A230*, 312.

(29) McWeeny, R.; Sutcliffe, B. T. *Methods of Molecular Quantum Mechanics*; Academic Press: London, New York, 1969; p 130.

Chart III



into account a limited configuration interaction (CI) with singly excited configurations. It is important to note that Brillouin's theorem applies only in a limited form to the restricted open-shell wave functions obtained by Roothaan's procedure.[30,31] This is due on the one hand to the more complex symmetry properties of open-shell wave functions,[30] which do not necessarily transform as the completely symmetric representation. On the other hand, even for configurations to which the limited Brillouin theorem as given by Manne[30] applies, another spin eigenfunction to the same singly excited configuration can be constructed that leads to a nonvanishing matrix element with the ground state.[31] It is exactly the configuration interaction with singly excited states resulting from the violation of the Brillouin theorem we have to consider if we wish to restore the spin polarization effect in the restricted Hartree–Fock method.

Now we want to consider the limited CI in the particular case of ferrocenium. This will be done in second-order perturbation theory. The singly excited states we are looking for have of course to be of E_{2g} symmetry. Considering the frontier orbitals including the e_{1u} orbitals not shown in Chart II, there are only two excitations that can result in a $^2E_{2g}$ singly excited state. These are obtained if we promote either an electron from e_{2g} or from e_{1g} to one of the e_{1g}* orbitals. Only the latter excitation shown in Chart III is of importance in our case. We will see later from the structure of the spin polarization term that the covalent character of the orbitals involved in the excitation is crucial if we want to describe the spin polarization between Fe and the Cp rings. This condition is not fulfilled for an excitation from the e_{2g} orbitals nor for any other excitation apart from $e_{1g} \rightarrow e_{1g}^*$.

Let us first consider the degenerate ground-state wave functions

$$|^2E_{2g}^{0,1}\rangle = |a\bar{a}b\bar{b}c\bar{c}d\rangle$$

$$|^2E_{2g}^{0,2}\rangle = |a\bar{a}b\bar{b}c\bar{d}d\rangle \tag{7}$$

For reasons of lucidity, we have included only the orbitals shown in Chart II, but eqs 7 nevertheless symbolize the full Slater determinants. We now have to find the correct symmetry-adapted $^2E_{2g}$ singly excited states for the configuration shown in Chart III. There are two of them, one of which can be found rather easily. Let us consider a ground-state wave function of say symmetry Γ_α for an arbitrary open-shell molecule. From this wave function, we construct a singly excited wave function by summing over all states with an electron excited from an orbital of a fully occupied degenerate set of symmetry, say Γ_β, to its equivalent partner in an unoccupied orbital set also of symmetry Γ_β. It has been mentioned by Manne[30] that such an excited wave function necessarily belongs to the same equivalence class and irreducible representation Γ_α as the ground-state wave function from which it has been constructed. Let us illustrate this by considering the first of the ground-state wave functions 7 of symmetry E_{2g} (corresponds to Γ_α). The orbitals involved in the excitation shown in Chart III are of e_{1g} symmetry (corresponds to Γ_β). The excitations we have to consider are a → a* and b → b*. Following Manne, we then obtain, e.g., $|a\bar{a}^*b\bar{b}c\bar{c}d\rangle + |a\bar{a}b\bar{b}^*c\bar{c}d\rangle$ from eqs 7 if we transfer the electron of spin β. This function has the same spatial symmetry E_{2g} as the ground state due to the fact that the sum of electron-hole functions aa* + bb* is completely symmetric. However, it is not a spin eigenfunction; it represents a mixture of doublet and quartet states. For a determinant with three singly occupied orbitals, there are two doublet spin functions for each magnetic quantum number obtained by the following linear combinations:[32]

$$|D_1(-\tfrac{1}{2})\rangle = \frac{1}{\sqrt{6}}(-2|\beta\beta\alpha\rangle + |\beta\alpha\beta\rangle + |\alpha\beta\beta\rangle)$$

$$|D_1(\tfrac{1}{2})\rangle = \frac{1}{\sqrt{6}}(2|\alpha\alpha\beta\rangle - |\alpha\beta\alpha\rangle - |\beta\alpha\alpha\rangle) \tag{8}$$

$$|D_2(-\tfrac{1}{2})\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\beta\rangle - |\beta\alpha\beta\rangle)$$

$$|D_2(\tfrac{1}{2})\rangle = \frac{1}{\sqrt{2}}(|\alpha\beta\alpha\rangle - |\beta\alpha\alpha\rangle)$$

Thus, we finally obtain the following singly excited wave functions of proper spatial and spin symmetry (only components with the magnetic quantum number $M_s = {}^1/_2$ are given):

$$|^2E_{2g}^{1,1}\rangle = \frac{1}{\sqrt{12}}(2|a\bar{d}b\bar{b}c\bar{c}a^*\rangle + |a\bar{a}^*b\bar{b}c\bar{c}d\rangle - |a^*\bar{a}b\bar{b}c\bar{c}d\rangle + 2|a\bar{a}b\bar{d}c\bar{c}b^*\rangle + |a\bar{a}b\bar{b}^*c\bar{c}d\rangle - |a\bar{a}b^*\bar{b}c\bar{c}d\rangle)$$

$$|^2E_{2g}^{1,2}\rangle = \frac{1}{\sqrt{12}}(2|a\bar{c}b\bar{b}a^*\bar{d}d\rangle + |a\bar{a}^*b\bar{b}c\bar{d}d\rangle - |a^*\bar{a}b\bar{b}c\bar{d}d\rangle + 2|a\bar{a}b\bar{c}b^*\bar{d}d\rangle + |a\bar{a}b\bar{b}^*c\bar{d}d\rangle - |a\bar{a}b^*\bar{b}c\bar{d}d\rangle) \tag{9}$$

$$|^2E_{2g}^{2,1}\rangle = \tfrac{1}{2}(|a\bar{a}^*b\bar{b}c\bar{c}d\rangle + |a^*\bar{a}b\bar{b}c\bar{c}d\rangle + |a\bar{a}b\bar{b}^*c\bar{c}d\rangle + |a\bar{a}b^*\bar{b}c\bar{c}d\rangle)$$

$$|^2E_{2g}^{2,2}\rangle = \tfrac{1}{2}(|a\bar{a}^*b\bar{b}c\bar{d}d\rangle + |a^*\bar{a}b\bar{b}c\bar{d}d\rangle + |a\bar{a}b\bar{b}^*c\bar{d}d\rangle + |a\bar{a}b^*\bar{b}c\bar{d}d\rangle)$$

We already mentioned that there is still another wave function of symmetry E_{2g} arising from the excitation $e_{1g} \rightarrow e_{1g}^*$ that, however, does not interact with the ground state and is therefore not considered any further. Moreover, the second set of wave functions in eqs 9 is subject to the restricted Brillouin theorem as given by Manne.[30] This can be verified by using the Slater–Condon rules for explicitly calculating the matrix elements with the ground state (eqs 7) and summing them over the two equivalence classes. If we also take into account the hermiticity of the projection operators and

$$\hat{R}_c'b = \hat{R}_c'a = 0 \qquad \hat{R}_e'b^* = \hat{R}_e'a^* = 0 \tag{10}$$

we can insert the Fock operator (eq 3) in the matrix element and obtain finally

$$\tfrac{1}{2}(\langle^2E_{2g}^{0,1}|\hat{H}|^2E_{2g}^{2,1}\rangle + \langle^2E_{2g}^{0,2}|\hat{H}|^2E_{2g}^{2,2}\rangle) = \langle a|\hat{F}|a^*\rangle + \langle b|\hat{F}|b^*\rangle = 0 \tag{11}$$

The matrix element is zero because a* and b* are of course eigenfunctions to the Hamiltonian $\hat{F}$ and orthogonal to a and b. It should also be noted that the two matrix elements on the left-hand side of eq 11 are equivalent for symmetry reasons and thus vanish individually. The summation over the equivalence classes is just a convenient means to obtain Roothaan's completely symmetric Hamiltonian, which has been derived by an analogous summation (see eq 2). Now let us form matrix elements between the ground state (eqs 7) and the first set of eqs 9. We obtain

$$\tfrac{1}{2}(\langle^2E_{2g}^{0,1}|\hat{H}|^2E_{2g}^{1,1}\rangle + \langle^2E_{2g}^{0,2}|\hat{H}|^2E_{2g}^{1,2}\rangle) = \frac{\sqrt{3}}{4}([ac|ca^*] + [bc|cb^*] + [ad|da^*] + [bd|db^*]) \equiv \frac{\sqrt{3}}{2}X \tag{12}$$

where we have introduced the abbreviation

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(30) Manne, R. *Mol. Phys.* **1972**, *24*, 935.
(31) Jungen, M. *Theor. Chim. Acta* **1968**, *11*, 193.
(32) Pauncz, R. *Spin Eigenfunctions*; Plenum Press: New York, 1979; p 19.

$$X = \tfrac{1}{2}([\mathrm{ac}|\mathrm{ca}^*] + [\mathrm{bc}|\mathrm{cb}^*] + [\mathrm{ad}|\mathrm{da}^*] + [\mathrm{bd}|\mathrm{db}^*]) \qquad (13)$$

The two-electron integrals are defined as usual:

$$[\mathrm{ab}|\mathrm{cd}] = \int \mathrm{a}^*(1)\mathrm{b}(1)\frac{e^2}{r_{12}}\mathrm{c}^*(2)\mathrm{d}(2)\,\mathrm{d}v_1\,\mathrm{d}v_2 \qquad (14)$$

The terms on the right-hand side of eq 13 are all of the same magnitude for symmetry reasons and can be considered as exchange integrals between an overlap density (aa* or bb*) and an electron density ($|\mathrm{c}|^2$ or $|\mathrm{d}|^2$).

Now we want to cast the matrix element 12 into a somewhat different form using explicitly the form of the MO's. We performed an extended Hückel calculation to obtain the MO's, but we want to emphasize that the qualitative features of these MO's are the same as for the ab initio SCF calculations available in the literature.[20] We already mentioned that the e_{2g} orbitals c and d are almost purely metal. It can be seen from Chart II that they correspond to $d_{x^2-y^2}$ and d_{xy} of Fe, respectively. The e_{1g} orbitals a,a* and b,b*, on the other hand, are a covalent mixture of orbitals from the metal and the Cp rings. a,b are Fe–Cp bonding whereas a*,b* are Fe–Cp antibonding (Chart II). These orbitals are split further into contributions from the individual Cp rings denoted by A and B. The MO's we are interested in can therefore be written as follows:

$$\mathrm{c} = \mathrm{d}_{x^2-y^2} \qquad \mathrm{d} = \mathrm{d}_{xy}$$

$$\mathrm{a} = c_1\mathrm{d}_{xz} + d_1\frac{1}{\sqrt{2}}(\pi_{\mathrm{A1}} + \pi_{\mathrm{B1}}) + \mathrm{Cp}\ \sigma\ \text{contributions}$$

$$\mathrm{b} = c_1\mathrm{d}_{yz} + d_1\frac{1}{\sqrt{2}}(\pi_{\mathrm{A2}} + \pi_{\mathrm{B2}}) + \mathrm{Cp}\ \sigma\ \text{contributions} \qquad (15)$$

$$\mathrm{a}^* = c_2\mathrm{d}_{xz} + d_2\frac{1}{\sqrt{2}}(\pi_{\mathrm{A1}} + \pi_{\mathrm{B1}}) + \mathrm{Cp}\ \sigma\ \text{contributions}$$

$$\mathrm{b}^* = c_2\mathrm{d}_{yz} + d_2\frac{1}{\sqrt{2}}(\pi_{\mathrm{A2}} + \pi_{\mathrm{B2}}) + \mathrm{Cp}\ \sigma\ \text{contributions}$$

π_{A1} and π_{A2} represent the degenerate π orbitals of e_1'' symmetry for Cp ring A (symmetry D_{5h}) with an analogous definition for Cp ring B. The e_{1g} π orbitals for the combined system of the two Cp rings are obtained by a proper linear combination of the individual e_1'' orbitals of ring A and B as indicated in eqs 15 (see also Chart II). The σ contributions on the Cp rings are small and will be neglected in the following. When eqs 15 are used and the differential overlap between orbitals on different atoms is neglected, only one-center exchange integrals are left in eq 13. We obtain

$$X = \tfrac{1}{2}c_1c_2([\mathrm{d}_{xz}\mathrm{d}_{x^2-y^2}|\mathrm{d}_{x^2-y^2}\mathrm{d}_{xz}] + [\mathrm{d}_{yz}\mathrm{d}_{x^2-y^2}|\mathrm{d}_{x^2-y^2}\mathrm{d}_{yz}] + [\mathrm{d}_{xz}\mathrm{d}_{xy}|\mathrm{d}_{xy}\mathrm{d}_{xz}] + [\mathrm{d}_{yz}\mathrm{d}_{xy}|\mathrm{d}_{xy}\mathrm{d}_{yz}]) \qquad (16)$$

The energy stabilization arising from the mixing just described is given by a second-order perturbation theory term:

$$\Delta E = \frac{|\langle {}^2\mathrm{E}^{0,1}_{2g}|\hat{H}|{}^2\mathrm{E}^{1,1}_{2g}\rangle + \langle {}^2\mathrm{E}^{0,2}_{2g}|\hat{H}|{}^2\mathrm{E}^{1,2}_{2g}\rangle|^2}{4U} = \frac{\tfrac{3}{4}X^2}{U} \qquad (17)$$

where U is the energy difference between the ground and the excited state:

$$U = E({}^2\mathrm{E}^1_{2g}) - E({}^2\mathrm{E}^0_{2g}) \qquad (18)$$

The corresponding wave function in first-order perturbation theory can be written as

$$|{}^2\mathrm{E}^1_{2g}\rangle = |{}^2\mathrm{E}^{0,1}_{2g}\rangle - \frac{\sqrt{3/4}\,X}{U}|{}^2\mathrm{E}^{1,1}_{2g}\rangle \qquad (19)$$

with an analogous expression for the second component of the degenerate set. Of course, there are more excited states to mix with the ground state, which in principal would have to be included in eq 19. But these do not contribute to the spin polarization between Fe and Cp in first order and will therefore be disregarded.

Now let us consider the spin density of the open-shell cation ferrocenium and how it is affected by the configurational mixing just described. Without configurational mixing, it is obvious that the spin density is given by the radical electron density $|\mathrm{d}|^2$ or $|\mathrm{c}|^2$ for the first or second of the degenerate ground-state wave functions 7, respectively. Since these orbitals are of metal character, we obtain a positive spin density on the metal and zero spin density on the Cp rings. This simple picture is changed if we consider the perturbed wave function 19. For the calculation of the spin density, the following spin density operator is used:

$$\hat{\rho}_s(\vec{R}) = 2\sum_i \hat{s}_{z,i}\delta(\vec{r}_i - \vec{R}) \qquad (20)$$

The sum runs over all electrons. $\delta(\vec{r}_i - \vec{R})$ is the δ function. $\hat{s}_{z,i}$ is the z component of the spin operator for electron i. To obtain the spin density for the wave function 19, we form the following matrix element:

$$\rho_s(\vec{R}) = \langle {}^2\mathrm{E}^1_{2g}|\hat{\rho}_s(\vec{R})|{}^2\mathrm{E}^1_{2g}\rangle \qquad (21)$$

Note that we consider only the first component (eq 19) of the degenerate set. Substituting eqs 7 and 9 into eq 19 and neglecting second order terms X^2/U^2, we obtain from eq 21

$$\rho_s(\vec{R}) = |\mathrm{d}(\vec{R})|^2 + \frac{X}{U}(\mathrm{a}^*(\vec{R})\mathrm{a}(\vec{R}) + \mathrm{b}^*(\vec{R})\mathrm{b}(\vec{R})) \qquad (22)$$

The first term of eq 22 is just the radical electron density of a single electron in orbital d, i.e., the contribution without configurational mixing. The second term that results from the configurational mixing does not have the usual form of a charge density but is given by an overlap density involving the orbitals of the excitation (aa* and bb*). Again we use eqs 15 to decompose the overlap densities into Fe and Cp contributions. Neglecting the small σ contributions on the Cp rings, we obtain

$$\mathrm{aa}^* = c_1c_2|\mathrm{d}_{xz}|^2 + \tfrac{1}{2}\,d_1d_2(|\pi_{\mathrm{A1}}|^2 + |\pi_{\mathrm{B1}}|^2)$$

$$\mathrm{bb}^* = c_1c_2|\mathrm{d}_{yz}|^2 + \tfrac{1}{2}\,d_1d_2(|\pi_{\mathrm{A2}}|^2 + |\pi_{\mathrm{B2}}|^2) \qquad (23)$$

Here we have omitted the argument $\vec{R}$. Inserting eqs 23 in eq 22, we finally obtain

$$\rho_s = |\mathrm{d}|^2 + \frac{X}{U}(c_1c_2(|\mathrm{d}_{xz}|^2 + \mathrm{d}_{yz}|^2) + \tfrac{1}{2}\,d_1d_2(|\pi_{\mathrm{A1}}|^2 + |\pi_{\mathrm{B1}}|^2 + |\pi_{\mathrm{A2}}|^2 + |\pi_{\mathrm{B2}}|^2)) \qquad (24)$$

Let us examine this expression in some more detail. First, we have to agree on a convention for the phase relations of the MO coefficients for the MO's a,b and a*,b*. We assume that the Fe contributions of these MO's represented by c_1 and c_2 in eqs 15 are of the same sign. It follows immediately from eq 16 that the matrix element X is then positive. Due to the orthogonality of the MO's a and a* (b and b*), it also follows that the Cp contributions represented by d_1 and d_2 in eqs 15 have to be of opposite sign. We already mentioned that a,b and a*,b* are Fe–Cp bonding and antibonding, respectively. Now it is seen easily that the additional term arising from configurational mixing on the right-hand side of eq 24 adds a positive spin density to the metal ($c_1c_2 > 0$) and a negative one to the Cp rings ($d_1d_2 < 0$). Thus, we have shown in a qualitative manner that there is a spin polarization effect leading to a negative spin density on the Cp rings. We only had to make some assumptions about the qualitative features of the MO's, which can be obtained easily from an extended Hückel calculation. The negative spin densities on the Cp rings of ferrocenium have also been observed in EPR and NMR experiments.[33] The role of this effect in the ferromagnetic coupling mechanism of DMFcTCNE will be discussed in the next section.

We want to finish this section by giving a rough numerical estimate of some of the quantities occuring in the preceding

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[33] (a) Materikova, R. B.; Babin, V. N.; Solodovnikov, S. P.; Lyatifov, I. R.; Petrovsky, P. V.; Fedin, E. I. *Z. Naturforsch.* **1980**, *35b*, 1415. (b) Köhler, F. H. Unpublished results.

discussion. First, we performed an extended Hückel calculation[19] in order to obtain the MO coefficients of eqs 15. With the parameters given in the Appendix, we find

$$c_1 = 0.525 \qquad c_2 = 0.887 \qquad d_1 = 0.734 \qquad d_2 = -0.723 \tag{25}$$

The exchange integrals in eq 16 can be evaluated by using Kotanis tables[34] and assuming that we are dealing with Slater orbitals, e.g.

$$[d_{xz}d_{xy}|d_{xy}d_{xz}] = 0.326\zeta\ (\mathrm{eV}) \tag{26}$$

where ζ is the Slater exponent. Usually one uses a double-ζ expansion for d orbitals. This complicates the evaluation of the exchange integral. The Slater exponents used in our extended Hückel calculation are 2.1 and 5.35. Inserting these values in eq 26, we obtain values of 0.7 and 1.75 eV. The actual value lies somewhere in between. In any case, the order of magnitude is 1 eV, which is a large value for an exchange integral. This is due to the contracted nature of the Fe 3d orbitals. Thus, we obtain a large mixing matrix element between the ground state and the excited state $e_{1g} \rightarrow e_{1g}{}^*$. Using eqs 16 and 25, we find 0.65 eV $< X <$ 1.6 eV.

A rough estimate of the energy difference U between the excited state and the ground state of ferrocenium can be obtained by just taking the difference in the orbital energies between e_{1g} and $e_{1g}{}^*$. Our extended Hückel calculation gives a value of ~4 eV, which is in accordance with another extended Hückel calculation reported previously.[35] From the spectroscopic data,[36] no direct information is available for the symmetry-forbidden transition $e_{1g} \rightarrow e_{1g}{}^*$. There are three optical absorption bands at 35 000, 40 000, and 50 000 cm^{-1} (~4.4–6.3 eV) for ferrocenium that Sohn et al.[36] ascribe to ligand–metal charge-transfer transitions $e_{1u} \rightarrow e_{1g}{}^*$. We did not include the e_{1u} orbitals in Chart II, but they are very close in energy to the e_{1g} orbitals. Thus, the energies of the transitions $e_{1g} \rightarrow e_{1g}{}^*$ might not be that different from those of $e_{1u} \rightarrow e_{1g}{}^*$. A value of U = 5 eV therefore seems to be a reasonable choice.

Now we can estimate the negative spin density on the Cp rings. Of course we cannot provide an accurate number that must be left for quantitative methods, but we can get an idea about the magnitude of the spin polarization effect. With X = 1 eV, U = 5 eV, and eqs 24 and 25, we obtain for the negative spin density on the two Cp rings

$$\rho_s(\mathrm{Cp}) \approx -0.2 \tag{27}$$

We already mentioned that the permethylation diminishes the gap between the Cp π and the Fe d orbitals. The valence ionization potentials obtained from photoelectron spectroscopy[23] suggest a reduction of this gap by ~0.5 eV. The energy difference between e_{1g} and $e_{1g}{}^*$ will also be reduced although less strongly because the $e_{1g}{}^*$ orbitals have considerable contributions from the Cp rings. But the permethylation not only reduces U, it also increases the mixing matrix element X because the enhanced covalent character of the orbitals a and a* (b and b*) will increase the product of the orbital coefficients c_1c_2 and d_1d_2 occuring in eqs 16 and 24. We recognize that the permethylation will affect X, U, and the orbital coefficient products in eq 24 in such a way as to increase the negative spin density. This is difficult to quantify within our approach because as we already mentioned we cannot rely too much on the extended Hückel results as far as the permethylation effect is concerned.

4. Spin Coupling in a Donor–Acceptor Pair

So far we only considered the ferrocenium ion with $S = {}^1/_2$. In the following, we will include one of the TCNE neighbors, thus singling out one donor–acceptor pair from the stack. In this respect, our procedure is analogous to the one of McConnell.[12] If there is ferromagnetic coupling for one donor–acceptor pair, it will occur for any such pair and, thus, throughout the stack.

The TCNE$^-$ ion is also an open-shell system with $S = {}^1/_2$. Its single electron is in the π^* orbital. We combine the wave functions of DMFc$^+$ ($S = {}^1/_2$) and TCNE$^-$ ($S = {}^1/_2$) to form a common wave function with $S = 0$ or $S = 1$ for the donor–acceptor pair. This is in some sense analogous to a valence bond approach where the wave function of a molecule is constructed from individual localized orbitals of the constituent atoms. The localized orbitals in our case, however, are MO's instead of AO's. In the following, we will consider only the first component of a $^2E_{2g}$ degenerate pair. Extending eqs 7, we obtain for the singlet and triplet ground states of the combined donor–acceptor system

$$|^3\mathrm{GS}\rangle = |\mathrm{a}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\pi^*\rangle \tag{28}$$

$$|^1\mathrm{GS}\rangle = \frac{1}{\sqrt{2}}(|\mathrm{a}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\bar{\pi}^*\rangle + |\mathrm{a}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\,\pi^*\bar{\mathrm{d}}\rangle)$$

Here we use again an abbreviated notation for the full Slater determinant of the combined donor–acceptor system. GS denotes the ground state. We dropped the symmetry labels because the combined donor–acceptor system no longer has D_{5d} symmetry. Now we form the combined donor–acceptor wave functions for the singly excited state considered in the previous section. Since we have four singly occupied orbitals, the formation of the correct spin functions is somewhat more complicated. We obtain a singlet or triplet from a doublet by subtraction or addition, respectively, of another doublet. Using the doublet wave functions 8 and the addition and subtraction formula for spin functions,[32] we obtain the following spin eigenfunctions for the singlet and triplet (only the component with $M_s = 1$ is given):

$$|\mathrm{T}_1(1)\rangle = |\mathrm{D}_1(\tfrac{1}{2})\rangle|\alpha\rangle = \frac{1}{\sqrt{6}}(2|\alpha\alpha\beta\alpha\rangle - |\alpha\beta\alpha\alpha\rangle - |\beta\alpha\alpha\alpha\rangle)$$

$$|\mathrm{S}_1\rangle = \frac{1}{\sqrt{2}}(|\mathrm{D}_1(\tfrac{1}{2})\rangle|\beta\rangle - |\mathrm{D}_1(-\tfrac{1}{2})\rangle|\alpha\rangle) = \frac{1}{\sqrt{12}}(2|\alpha\alpha\beta\beta\rangle + 2|\beta\beta\alpha\alpha\rangle - |\alpha\beta\alpha\beta\rangle - |\beta\alpha\beta\alpha\rangle - |\beta\alpha\alpha\beta{<}{<}\mathrm{rb} - |\alpha\beta\beta\alpha\rangle) \tag{29}$$

It should be noted that we consider only the first pair of doublet functions of eqs 8 because in the previous section only this function gave rise to a nonvanishing matrix element with the ground state. Attaching the orbital π^* to the corresponding wave function in eqs 9 and using eqs 29, we obtain the following singlet and triplet singly excited states:

$$|^3\mathrm{ES}\rangle = \frac{1}{\sqrt{12}}(2|\mathrm{a}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{d}}\mathrm{c}\bar{\mathrm{c}}\mathrm{b}^*\pi^*\rangle + |\mathrm{a}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}^*\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\pi^*\rangle - |\mathrm{a}\bar{\mathrm{a}}\mathrm{b}^*\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\pi^*\rangle + 2|\mathrm{a}\bar{\mathrm{d}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{a}^*\pi^*\rangle + |\mathrm{a}\bar{\mathrm{a}}^*\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\pi^*\rangle - |\mathrm{a}^*\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\pi^*\rangle) \tag{30}$$

$$\begin{aligned}|^1\mathrm{ES}\rangle = \frac{1}{\sqrt{24}}(&2|\mathrm{a}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{d}}\mathrm{c}\bar{\mathrm{c}}\mathrm{b}^*\bar{\pi}^*\rangle + |\mathrm{a}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}^*\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\bar{\pi}^*\rangle - |\mathrm{a}\bar{\mathrm{a}}\mathrm{b}^*\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\bar{\pi}^*\rangle + \\ &2|\mathrm{a}\bar{\mathrm{d}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{a}^*\bar{\pi}^*\rangle + |\mathrm{a}\bar{\mathrm{a}}^*\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\bar{\pi}^*\rangle - |\mathrm{a}^*\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\mathrm{d}\bar{\pi}^*\rangle + \\ &2|\mathrm{a}\bar{\mathrm{a}}\mathrm{d}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\pi^*\bar{\mathrm{b}}^*\rangle + |\mathrm{a}\bar{\mathrm{a}}\mathrm{b}^*\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\pi^*\bar{\mathrm{d}}\rangle - |\mathrm{a}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}^*\mathrm{c}\bar{\mathrm{c}}\pi^*\bar{\mathrm{d}}\rangle + \\ &2|\mathrm{d}\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\pi^*\bar{\mathrm{a}}^*\rangle + |\mathrm{a}^*\bar{\mathrm{a}}\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\pi^*\bar{\mathrm{d}}\rangle - |\mathrm{a}\bar{\mathrm{a}}^*\mathrm{b}\bar{\mathrm{b}}\mathrm{c}\bar{\mathrm{c}}\pi^*\bar{\mathrm{d}}\rangle)\end{aligned}$$

Like in the previous section for the donor alone, we now form matrix elements between ground- and excited-state wave functions for the combined donor–acceptor system. Since the orbitals are assumed to have been determined self-consistently for the individual donor and acceptor, we now have to deal with nonorthogonal orbitals. In fact, we will see in a moment that a nonvanishing overlap integral between donor and acceptor orbitals is essential for our mechanism. But it renders the calculation of matrix elements difficult because it prevents us from using the Slater–Condon rules. A general scheme for the calculation of matrix elements between Slater determinants consisting of nonorthogonal orbitals has been developed by Löwdin.[37] In the following, we

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(34) Kotani, M.; Amemiya, A.; Ishiguro, E.; Kimura, T. *Table of molecular integrals*; Maruzen Co. Ltd.: Tokyo, 1963.

(35) Kirchner, R. F.; Loew, G. H.; Mueller-Westerhoff, U. T. *Theor. Chim. Acta* **1976**, *41*, 1.

(36) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

(37) Löwdin, P. O. *Phys. Rev.* **1955**, *97*, 1474.

will neglect any overlap populations of higher than second order. We obtain the following matrix elements:

$$\langle {}^3\mathrm{GS}|\hat{H}|{}^3\mathrm{ES}\rangle = \frac{\sqrt{3}}{2}(X + \tfrac{1}{3}([\mathrm{b}\pi^*|\pi^*\mathrm{b}^*] + [\mathrm{a}\pi^*|\pi^*\mathrm{a}^*] + \langle \mathrm{b}|\hat{F}_{\mathrm{core}}|\pi^*\rangle\langle\pi^*|\mathrm{b}^*\rangle + \langle\pi^*|\hat{F}_{\mathrm{core}}|\mathrm{b}^*\rangle\langle \mathrm{b}|\pi^*\rangle + \langle \mathrm{a}|\hat{F}_{\mathrm{core}}|\pi^*\rangle\langle\pi^*|\mathrm{a}^*\rangle + \langle\pi^*|\hat{F}_{\mathrm{core}}|\mathrm{a}^*\rangle\langle \mathrm{a}|\pi^*\rangle)) \quad (31)$$

$$\langle {}^1\mathrm{GS}|\hat{H}|{}^1\mathrm{ES}\rangle = \frac{\sqrt{3}}{2}(X - ([\mathrm{b}\pi^*|\pi^*\mathrm{b}^*] + [\mathrm{a}\pi^*|\pi^*\mathrm{a}^*] + \langle \mathrm{b}|\hat{F}_{\mathrm{core}}|\pi^*\rangle\langle\pi^*|\mathrm{b}^*\rangle + \langle\pi^*|\hat{F}_{\mathrm{core}}|\mathrm{b}^*\rangle\langle \mathrm{b}|\pi^*\rangle + \langle \mathrm{a}|\hat{F}_{\mathrm{core}}|\pi^*\rangle\langle\pi^*|\mathrm{a}^*\rangle + \langle\pi^*|\hat{F}_{\mathrm{core}}|\mathrm{a}^*\rangle\langle \mathrm{a}|\pi^*\rangle))$$

The operator $\hat{F}_{\mathrm{core}}$ refers to the combined donor–acceptor system and contains the one-electron part of the Hamiltonian and all two-electron Coulomb and exchange operators except those of the radical electrons. Of course, the matrix element found for the donor alone (eq 12) must reappear in the expression for the combined donor–acceptor system. This is the term X on the right-hand side of eqs 31. But now there are additional terms resulting from the donor–acceptor interaction or, to put it more precisely, from a particle exchange between the charge density $|\pi^*|^2$ of the radical electron on TCNE and the overlap density aa* or bb* on DMFc. It is these terms that make the difference between singlet and triplet. We introduce the following abbreviations:

$$Y = [\mathrm{b}\pi^*|\pi^*\mathrm{b}^*] + [\mathrm{a}\pi^*|\pi^*\mathrm{a}^*]$$

$$Z = \langle \mathrm{b}|\hat{F}_{\mathrm{core}}|\pi^*\rangle\langle\pi^*|\mathrm{b}^*\rangle + \langle\pi^*|\hat{F}_{\mathrm{core}}|\mathrm{b}^*\rangle\langle \mathrm{b}|\pi^*\rangle + \langle \mathrm{a}|\hat{F}_{\mathrm{core}}|\pi^*\rangle\langle\pi^*|\mathrm{a}^*\rangle + \langle\pi^*|\hat{F}_{\mathrm{core}}|\mathrm{a}^*\rangle\langle \mathrm{a}|\pi^*\rangle \quad (32)$$

Using eqs 15, we can decompose a and a* (b and b*) into metal and Cp contributions in a manner that is completely analogous to the one applied in the previous section. Since any overlap falls off rapidly with increasing distance of the overlapping orbitals, we can neglect overlap densities between metal and TCNE orbitals as compared to overlap densities between Cp and TCNE orbitals. Note that one of the Cp rings is considerably closer to the neighboring TCNE molecule than the Fe atoms (3.5 Å vs 5 Å). Let us assume that it is Cp ring A which is adjacent to the TCNE molecule of the donor–acceptor pair. We will of course also neglect overlap densities between TCNE and the more distant Cp ring. Using this argument, we can neglect the contributions from the metal and Cp ring B in eqs 15 and obtain from eqs 32

$$Y = \tfrac{1}{2}\, d_1 d_2([\pi_{\mathrm{A1}}\pi^*|\pi^*\pi_{\mathrm{A1}}] + [\pi_{\mathrm{A2}}\pi^*|\pi^*\pi_{\mathrm{A2}}]) \quad (33)$$

$$Z = \tfrac{1}{2}\, d_1 d_2(2\langle\pi_{\mathrm{A1}}|\hat{F}_{\mathrm{core}}|\pi^*\rangle\langle\pi^*|\pi_{\mathrm{A1}}\rangle + 2\langle\pi_{\mathrm{A2}}|\hat{F}_{\mathrm{core}}|\pi^*\rangle\langle\pi^*|\pi_{\mathrm{A2}}\rangle)$$

Using the abbreviation (eqs 32), we can write the matrix elements (eqs 31) in a more compact form:

$$\langle {}^3\mathrm{GS}|\hat{H}|{}^3\mathrm{ES}\rangle = \frac{\sqrt{3}}{2}(X + \tfrac{1}{3}(Y + Z)) \quad (34)$$

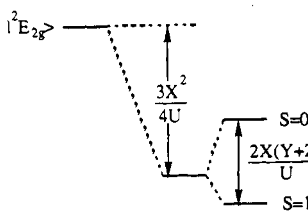
$$\langle {}^1\mathrm{GS}|\hat{H}|{}^1\mathrm{ES}\rangle = \frac{\sqrt{3}}{2}(X - (Y + Z))$$

The energy stabilization terms arising from this mixing are again obtained by second-order perturbation theory. The energy denominator is given by eq 18. We obtain

$$\Delta E_{\mathrm{T}} = \frac{|\langle {}^3\mathrm{GS}|\hat{H}|{}^3\mathrm{ES}\rangle|^2}{U} = \frac{\tfrac{3}{4}(X + \tfrac{1}{3}(Y + Z))^2}{\mathrm{U}} \approx \frac{\tfrac{3}{4}X^2 + \tfrac{1}{2}X(Y + Z)}{U} \quad (35)$$

$$\Delta E_{\mathrm{s}} = \frac{|\langle {}^1\mathrm{GS}|\hat{H}|{}^1\mathrm{ES}\rangle|^2}{U} = \frac{\tfrac{3}{4}(X - (Y + Z))^2}{U} \approx \frac{\tfrac{3}{4}X^2 - \tfrac{3}{2}X(Y + Z)}{U}$$

Chart IV



Here we used $|Y|$ and $|Z| \ll X$. This is based on the fact that Y and Z contain donor–acceptor overlap densities in second order. Due to the considerable intermolecular distances, these overlap densities can be expected to be very small. X, on the other hand, is comprised of one-center integrals (eq 16). Now we can calculate the energy difference between singlet and triplet:

$$\Delta E_{\mathrm{ST}} = E_{\mathrm{S}} - E_{\mathrm{T}} = -(\Delta E_{\mathrm{S}} - \Delta E_{\mathrm{T}}) = \frac{2X(Y + Z)}{U} \quad (36)$$

A schematic energy level scheme is shown in Chart IV. It should be noted that the magnitudes of the energy terms are not represented properly in Chart IV. The first term given by eq 17 is much larger than the second (eq 36). Please note that the energy stabilization terms have to be taken with a negative sign. The factor X/U in eq 36 is a consequence of the perturbation theory treatment. The singlet–triplet energy difference is caused by the term $Y + Z$ to which we will direct our attention in the following. It is very illustrative to compare this term with another term frequently encountered in the discussion of ferro- or antiferromagnetic couplings,[38] which occured as early as in the valence bond treatment of Heitler–London for the H_2 molecule. The singlet–triplet energy splitting $2K$ in H_2 is given by an exchange integral that can be written as follows:[39]

$$K = [\mathrm{ab}|\mathrm{ba}] + 2\langle \mathrm{a}|\hat{h}|\mathrm{b}\rangle\langle \mathrm{b}|\mathrm{a}\rangle \quad (37)$$

a and b are the H 1s orbitals on the two centers. A remark with respect to the terminology is appropriate at this point. Although very often the complete expression 37 is denoted as an exchange integral, we wish to reserve this designation for the two-electron integral on the right-hand side of eq 37 as we did already in the preceding part of this paper. K comprises two contributions of opposite sign: a ferromagnetic one given by the exchange integral [ab|ba], which is always positive, and an antiferromagnetic one given by the product of the overlap and the resonance integral, which is always negative, because the two integrals are necessarily of opposite sign. A more detailed discussion can be found in ref 38. The term 37 is of some general significance in magnetic problems. In most cases, the antiferromagnetic term dominates. Ferromagnetic coupling is restricted mainly to those cases where the orbitals a and b are orthogonal due to symmetry reasons so that the overlap integral between them vanishes.[9,38]

If we look at the term $Y + Z$ (eqs 32) carefully, we recognize that its structure is completely analogous to eq 37. It also comprises an exchange integral (Y) and products of overlap and resonance integrals (Z). There is an important difference, however; in eq 37, the particle exchange takes place between the charge densities $|\mathrm{a}|^2$ and $|\mathrm{b}|^2$ whereas in our case we are faced with an exchange between a charge density $|\pi^*|^2$ and an *overlap density* aa* or bb*. This is also the reason why we have two different products of resonance and exchange integrals in Z instead of the factor 2 in eq 37. When the overlap densities aa* and bb* are decomposed into Cp and metal contributions and the latter is neglected as has been done in eqs 33, the structural similarity becomes even more obvious. Equations 33 reveal another dif-

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(38) (a) Girerd, J. J.; Journaux, Y.; Kahn, O. *Chem. Phys. Lett.* **1981**, *82*, 534. (b) Kahn, O.; Charlot, M. F. In *Valence Bond Theory and Chemical Structure*; Klein, D. J., Trinajstic, N., Eds.; Elsevier: Amsterdam, 1990; p 489.

(39) McWeeny, R.; Sutcliffe, B. T. *Methods of Molecular Quantum Mechanics*: Academic Press: London, New York, 1969; p 151.

ference; as a consequence of the phase relations of the MO coefficients of the orbitals a and a*, the signs of Y and Z are inverted as compared to the corresponding terms in the Heitler–London case. We have seen in the previous section that the phase factors of a and a* have been chosen in such a way that the metal contributions are of the same sign, whereas the Cp contributions are of opposite sign, leading to a negative product d_1d_2 (eqs 15 and 25). From eqs 33, it can be seen that this results in a positive Z and a negative Y. Note that the product of a resonance with the corresponding overlap integral is always negative. Thus, if $|Z| > |Y|$, i.e., if the resonance–overlap term Z dominates over the exchange term Y, the energy splitting (eq 36) will be positive, resulting in a triplet ground state, i.e., ferromagnetic coupling. The same condition leads to antiferromagnetic coupling in the Heitler–London term 37. Z and Y can therefore be denoted as ferromagnetic and antiferromagnetic contributions to the spin coupling constants, respectively.

We can go even further in our interpretation. So far our considerations have been based mainly on energy differences, and we just discovered some structural similarity between the singlet–triplet energy splitting term in our case and the valence bond term 37. The latter arises from particle exchange between the charge densities of the orbitals involved. Where are the relevant densities in our case? For TCNE, the answer is simple; it is of course the radical electron density $|\pi^*|^2$. For ferrocenium, we have to consider the spin density ρ_s we calculated in the previous section (eq 22). Let us form an exchange term K' between the ferrocenium spin density ρ_s and the TCNE spin density $|\pi^*|^2$. The procedure is completely analogous to the one of Heitler–London leading to the expression 37. The Hamiltonian used for forming the matrix element consists of $\hat{F}_{\text{core}}$, which in addition to the interaction with the nuclei also contains the interaction with the electrons assigned to the core, and the Coulomb repulsion term e^2/r_{12} for the two electrons considered explicitly. Using eq 22, we obtain the following exchange term:

$$\begin{aligned} K' = {} & \langle \mathrm{d}(1)\pi^*(2)|\hat{F}_{\text{core}}(1) + \hat{F}_{\text{core}}(2) + \frac{e^2}{r_{12}}|\pi^*(1)\mathrm{d}(2)\rangle + \\ & \frac{X}{U}\langle \mathrm{b}(1)\pi^*(2)|\hat{F}_{\text{core}}(1) + \hat{F}_{\text{core}}(2) + \frac{e^2}{r_{12}}|\pi^*(1)\mathrm{b}^*(2)\rangle + \\ & \frac{X}{U}\langle \mathrm{a}(1)\pi^*(2)|\hat{F}_{\text{core}}(1) + \hat{F}_{\text{core}}(2) + \frac{e^2}{r_{12}}|\pi^*(1)\mathrm{a}^*(2)\rangle \end{aligned} \tag{38}$$

The first term on the right-hand side of eq 38 is just the usual Heitler–London term for the exchange interaction of an electron in orbital d and another one in π^*. It can be neglected because it contains overlap densities between the orbital d, which is purely metal, and π^*. We already mentioned that we retain only donor–acceptor overlap populations between orbitals on TCNE and the adjacent Cp ring due to their closer distance. The expression 38 then can be written as follows:

$$\begin{aligned} K' = \frac{X}{U}(& \langle \mathrm{b}|\hat{F}_{\text{core}}|\pi^*\rangle\langle\pi^*|\mathrm{b}^*\rangle + \langle\pi^*|\hat{F}_{\text{core}}|\mathrm{b}^*\rangle\langle \mathrm{b}|\pi^*\rangle + \\ & \langle \mathrm{a}|\hat{F}_{\text{core}}|\pi^*\rangle\langle\pi^*|\mathrm{a}^*\rangle + \langle\pi^*|\hat{F}_{\text{core}}|\mathrm{a}^*\rangle\langle \mathrm{a}|\pi^*\rangle + \\ & [\mathrm{b}\pi^*|\pi^*\mathrm{b}^*] + [\mathrm{a}\pi^*|\pi^*\mathrm{a}^*]) \end{aligned} \tag{39}$$

Using the abbreviation 32, we obtain the more compact form

$$K' = \frac{X(Y + Z)}{U} \tag{40}$$

It is important to note that we derived this term independently from the preceding energy calculations by starting out with only the spin densities and using a Heitler–London-like formalism. Comparing eq 40 with the singlet–triplet energy splitting (eq 36), we obtain

$$\Delta E_{\text{ST}} = 2K' \tag{41}$$

Table I. Resonance and Overlap Integrals between the TCNE π^* and the Ferrocenium e_{1g} and $e_{1g}{}^*$ Orbitals

$\langle a\|\pi^*\rangle$	$\langle a^*\|\pi^*\rangle$	$\langle a\|h\|\pi^*\rangle$ (eV)	$\langle a^*\|h\|\pi^*\rangle$ (eV)
0.0095	−0.0075	−0.1977	0.1454

This is analogous to the Heitler–London model where the singlet–triplet splitting is also given by $2K$. We have already shown, however, that the sign of K' is inverted as compared to the Heitler–London case. That this sign inversal is really a consequence of the negative spin density on the Cp rings becomes obvious when we use the form 33 for Y and Z. We then obtain

$$\begin{aligned} K' = \tfrac{1}{2}\, d_1 d_2 \frac{X}{U}(& 2\langle\pi_{\mathrm{A}1}|\hat{F}_{\text{core}}|\pi^*\rangle\langle\pi^*|\pi_{\mathrm{A}1}\rangle + \\ & 2\langle\pi_{\mathrm{A}2}|\hat{F}_{\text{core}}|\pi^*\rangle\langle\pi^*|\pi_{\mathrm{A}2}\rangle + \\ & [\pi_{\mathrm{A}1}\pi^*|\pi^*\pi_{\mathrm{A}1}] + [\pi_{\mathrm{A}2}\pi^*|\pi^*\pi_{\mathrm{A}2}]) \end{aligned} \tag{42}$$

Considering the different contributions to the spin density (eq 24), we can see that only the negative contribution of Cp ring A "survives" in eq 42. Our mechanism can therefore be described as an exchange interaction between a negative spin density on the Cp rings and the radical electron density on TCNE. Thus, the spin coupling mechanism in DMFcTCNE corresponds to a model suggested some time ago by McConnell[7] as has already been pointed out by Buchachenko.[18]

In the Heitler–London model, the negative resonance–overlap term in eq 37 generally dominates over the exchange integral, leading to a negative sign of K and, thus, to a singlet ground state. Taking this as a general empirical rule for nonorthogonal, overlapping orbitals, we end up with a triplet ground state in our case due to the sign inversal of K'. We have seen that Z is the term that favors ferromagnetic interaction, whereas Y is the antiferromagnetic term.

It should be noted that both Y and Z will be very sensitive to the actual spatial arrangement of the acceptor relative to the donor. As the positions of the anions in the ferromagnetic phase of DMFcTCNE are not known due to their disorder,[15] the crucial parameters Y and Z will escape an exact numerical evaluation even if proper computational means are available. One qualitative statement, however, is still possible. If we refer to the symmetric geometrical arrangement of Chart I, the overlap integrals $\langle \mathrm{b}|\pi^*\rangle$ and $\langle\pi^*|\mathrm{b}^*\rangle$ vanish for symmetry reasons. The symmetry of the combined donor–acceptor system is C_s with the yz plane as a symmetry plane (Chart I). It can be seen from Chart II that b and b* are symmetric with respect to this plane, whereas π^* is antisymmetric. As a consequence, the ferromagnetic term Z in eqs 32 will be diminished because two of the four summands vanish. Thus, the symmetric arrangement shown in Chart I is certainly not the most favorable one for ferromagnetic interaction.

The preceding considerations have been based on the assumption $|Y|,|Z| \ll X$. Although the quantities Y and Z cannot be calculated due to the lack of geometrical data, we would like to know their order of magnitude, which can be expected to be the same for both Y and Z. We therefore performed an extended Hückel calculation for a donor–acceptor pair with the symmetric arrangement shown in Chart I. The overlap integrals necessary for an evaluation of Z (eqs 32) are obtained directly from the extended Hückel calculation. They are given in Table I. To obtain the matrix elements also contained in Z, we replace the Fock Hamiltonian $\hat{F}_{\text{core}}$ by the effective one-electron Hamiltonian of the extended Hückel scheme. This is, of course, a very crude procedure, but it should provide us with the correct order of magnitude. Although the extended Hückel Hamiltonian does not contain explicitly the electron–electron interaction, this interaction must be contained in some global manner in the parameterization of this semiempirical method. The matrix elements thus obtained can also be found in Table I. Substituting all these quantities in eqs 32, we finally obtain

$$Z \approx 3 \text{ meV} \tag{43}$$

It can be seen that Z is about 3 orders of magnitude smaller than X (~1 eV). It should also be noted that this order of magnitude is compatible with the experimentally determined coupling constant J, which amounts to 2.4 meV.[15]

5. Discussion

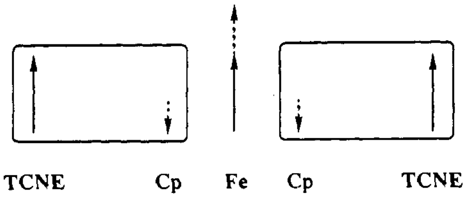
In the previous section, we have invoked configurational interaction with a singly excited ferrocenium state in order to explain the ferromagnetic coupling for a donor–acceptor pair. Several questions may have arisen in the readers mind. They are most easily discussed in hindsight. First of all, after having dismissed the McConnell mechanism, why is it necessary at all to refer to configurational mixing? And if so, why this peculiar choice of the excited state-configuration, which might seem somewhat arbitrary?

As to the first question, we are confronted with a problem of the order of magnitude. In any case of ferromagnetic or antiferromagnetic coupling, it is the overlap of the orbitals involved that is essential. For DMFc$^+$TCNE$^-$, we expect the direct coupling between the unpaired electron of ferrocenium, which is localized on the metal, and the one of TCNE$^-$ to be very weak. This is due to the large distance of ~5 Å between the metal and TCNE and also to the localized nature of the Fe d orbitals. Since the Cp rings are considerably closer to TCNE than the Fe atom, we had the idea that the Cp rings must be involved in the coupling mechanism. We have seen that the crucial matrix elements Y and Z (eqs 32) arise from an exchange interaction between the radical electron density on TCNE and an overlap density comprising the orbitals involved in the excitation ($a \rightarrow a^*$, $b \rightarrow b^*$). These latter orbitals both have considerable contributions from the Cp rings represented by the orbital coefficients d_1 (a,b) and d_2 (a*,b*) in eqs 15. It can be seen from eqs 33 that the matrix elements Y and Z are proportional to the product d_1d_2.

Now we are also able to understand why the covalent character of the orbitals involved in the excitation was necessary. We have just seen that these orbitals must have strong contributions on Cp. But they must also have strong contributions on the metal. This becomes obvious when we consider the matrix element X (eq 16). This is also an exchange integral arising from exchange between the same overlap densities as before (aa*,bb*) and the radical electron density $|d|^2$ or $|c|^2$ of the ferrocenium radical electron. If this exchange integral is to be large, the orbitals involved in the excitation must also have strong metal contributions represented by the coefficients c_1 and c_2 in eqs 15. It can be seen from eq 16 that the matrix element X is proportional to the coefficient product c_1c_2. This explains our particular choice of the excited configuration. The orbitals e_{1g} and e_{1g}^* are the only ones with contributions on both Fe and Cp. To summarize briefly, the overlap density arising from the excitation is involved in particle exchange with both the radical electron density on the metal and on TCNE. It is through this overlap density that the two radical electrons interact in our mechanism.

We have seen that even if we restrict ourselves to transitions $e_{1g} \rightarrow e_{1g}^*$, there is not just one excited state with the proper E_{2g} symmetry. From spatial symmetry considerations alone, we obtain two $^2E_{2g}$ pairs for the excited state. We can assign two doublet wave functions to each of them, ending up with four $^2E_{2g}$ excited states. We have shown in section 3 that only one of them actually mixes with the ferrocenium ground state, the mixing being determined by the parameter X. This holds for ferrocenium alone. For the combined donor–acceptor system, the states arising from the other $^2E_{2g}$ states can also mix with the ground state due to particle exchange between donor and acceptor. In principle, one would have to consider even the quartet state of the excited ferrocenium configuration because it can also couple with the TCNE doublet to give a triplet. Why did we disregard these possibilities in section 4? This is due to the structure of the perturbation theory terms 35. We have seen that matrix elements arising from particle exchange between donor and acceptor alone are of the order of millielectronvolts (eq 43). In the energy stabilization terms given by second-order perturbation theory, these matrix elements have to be squared so that the numerator is of the order 10^{-6} eV. In eqs 35, on the other hand, the large quantity X (~1 eV) is present in the numerator. Squaring these matrix elements, we obtain mixed terms of X and the matrix elements arising from donor–acceptor particle exchange. It can be seen from eq 36 that these mixed terms cause the singlet–triplet energy splitting. The numerator of eq 36 is of the order of 10^{-3} eV, 3 orders of magnitude larger than the numerator of the energy stabilization terms without X. Hence, it is sufficient to consider only the mixing with the excited-state configuration that gives rise to the presence of X in the mixing matrix element, i.e., the one that gives rise to the negative spin density on the Cp rings for a single ferrocenium ion.

Chart V



We have seen that the metal exchange integrals contained in X are roughly 1 eV, which is an unusually large value for an exchange integral. This is due to the contracted nature of the Fe d orbitals and provides for a strong mixing of ground and excited states. Thus, the strongly localized metal d radical electron, although not directly coupling to the TCNE radical electron, plays a crucial role. It would therefore be misleading to consider DMFc$^+$TCNE$^-$ as an "organic ferromagnet".

The configurational mixing invoked in the previous sections is due to the open-shell nature of ferrocenium. In neutral ferrocene, the matrix element for the same excitation would be zero due to the Brillouin theorem. It is the CI due to the violation of the Brillouin theorem in open-shell systems that accounts for the spin polarization in the restricted Hartree–Fock method. This leads to negative spin densities on the Cp rings in our case. Without this limited form of CI, we would have a positive spin density on the metal, whereas the spin density on Cp would be almost zero. Due to the exchange stabilization mentioned at the beginning of section 3, electrons of the same spin repel each other less strongly than electrons of different spin. Thus, the radical electron with spin α on the metal "attracts" additional density from the remaining electrons of the same spin; the spin density on the metal is enhanced, and as a consequence we are left with a negative spin density on the Cp rings that arises from an additional density of electrons with spin β. It should be noted that this is completely analogous to the well-known case of the allyl radical where the radical electron localized on the outer carbon atoms induces a negative spin density on the central carbon atom.[25] Concerning the magnitude of the spin polarization effect in DMFc$^+$TCNE$^-$, it is again the covalent character of the orbitals a,b and a*,b* that comes into play for the same reasons as given above. This can be seen from eq 24 where the product d_1d_2 enters directly into the Cp part of the spin density whereas the product c_1c_2 is contained in the matrix element X.

That various metallocene or metallocenium complexes are susceptible to this kind of spin polarization has already been noted on several occasions.[33,40,41] Levy and Orgel[41] presented an alternative view of the spin polarization effect. They consider the metal and the Cp rings as separate entities. The major charge-transfer process then takes place from the e_{1g} orbitals of Cp to a metal d orbital. What matters is the different electron affinity of the metal for electrons of different spin. In many cases, the spin of the transferred electron and the spin already present on the metal will be parallel, leaving behind an electron of opposite spin on the Cp ring. This simple model, however, neglects the covalent character of the e_{1g} orbitals, which is crucial in our mechanism.

We have derived an analytical expression for the negative Cp spin density and shown explicitly that the singlet–triplet splitting for a donor–acceptor pair can be described by particle exchange

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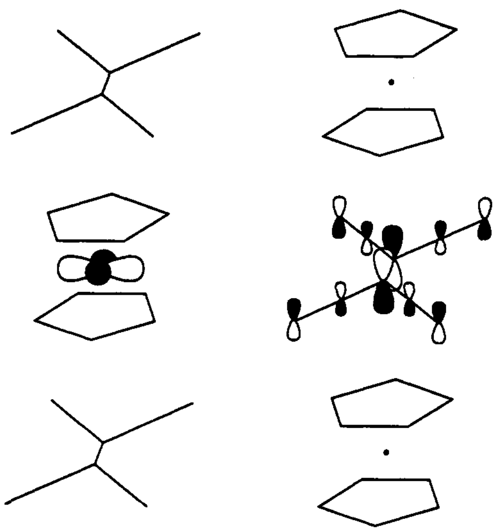
[40] Köhler, F. H.; Doll, K. H.; Prössdorf, W. *J. Organomet. Chem.* **1982**, *224*, 341.

[41] Levy, D. A.; Orgel, L. E. *Mol. Phys.* **1960**, *3*, 583.

Chart VI



between this negative spin density and the radical electron density on TCNE in complete analogy to the Heitler–London model. Thus, we end up with a very nice pictorial interpretation of our mechanism, which is illustrated in Chart V. The radical electron spins on Fe and TCNE are given by the arrows. The induced spin density on ferrocenium (positive on Fe, negative on Cp) resulting from the configurational mixing is symbolized by dashed arrows. We have encircled the coupling spins. To summarize briefly, we can describe our mechanism as follows: We have a radical electron spin on the Fe atom of ferrocenium that gives rise to the spin correlation effect just described by inducing a negative spin density on the Cp rings. This negative spin density interacts with the radical electron on TCNE by the usual exchange mechanism. The direct exchange between the spin on Fe and the one on TCNE can be neglected due to the larger distance between Fe and TCNE. It is interesting to note that, although we dismissed the McConnell mechanism[12] based on configurational mixing of a triplet excited state $DMFc^{2+}TCNE^{2-}$ with the ground state at the beginning of this paper, we finally end up with another idea of McConnell.[7] This model considers intermolecular coupling of organic radicals with alternating positive and negative spin densities on their carbon backbones. In order to obtain ferromagnetic coupling for two neighboring molecules, they have to be positioned in such a way that a site with positive spin density on one molecule is in registry with a site with negative spin density on the neighboring molecule. This mechanism has been confirmed nicely by EPR experiments for two triplet diphenyl carbenes incorporated in a paracyclophane skeleton.[42] Although this coupling mechanism was suggested in a different context, it is easily transferable to the case of $DMFc^+TCNE^-$. We already mentioned that this was done first by Buchachenko[18] who presented the basic idea without elaborating it in detail. It should be noted, however, that he assumes the negative spin densities to be on the methyl groups instead of the carbon atoms of the Cp ring. Obviously this is based on a misinterpretation of the experimental results.[33]

What is essential in our mechanism of spin polarization for $DMFc^+$ is the mixing of the ground configuration with the ligand–metal charge-transfer configuration $e_{1g}{}^3e_{2g}{}^3e_{1g}{}^*$. In absence of spin–orbit coupling and assuming that the symmetry is exactly D_{5d}, only one $^2E_{2g}$ state arising from this excited configuration couples with the ground state. If spin–orbit coupling is not ignored anymore,[43] then other excited states arising from the same excited configuration mix with the ground state, which may increase the negative spin density on the rings. These excited states are the spin doublet $^2E_{1g}$, but also the spin quartets $^4A_{1g}+{}^4A_{2g}+{}^4E_{1g}+2{}^4E_{2g}$. This effect of the spin–orbit coupling is certainly difficult to quantify. It should however be noted that neglecting spin–orbit coupling has essentially the same effect as idealizing the symmetry in D_{5d}; it underestimates the negative spin density on the rings.

So far we considered only the coupling within a donor–acceptor stack. In order to achieve bulk ferromagnetic behavior, a coupling mechanism between molecules in different stacks is also needed. This interaction will be much weaker than the intrastack coupling due to the large interstack distances. There are out-of-registry neighboring stacks in the crystal as is shown schematically in Chart VI. We have drawn the orbitals occupied by the radical electrons of a donor–acceptor pair in two neighboring stacks. It can be seen that they are orthogonal if the Fe atom is located in the plane of the TCNE molecule of the neighbor stack. Thus, we might refer to the well-known coupling term 37 in order to describe the ferromagnetic interstack coupling. a and b are now the orbitals shown in Chart VI. We already mentioned that the first term in eq 37, i.e., the exchange integral, ensures ferromagnetic interaction in case the overlap integral of the second term vanishes for symmetry reasons. Even if the overlap integral is not exactly zero because the real geometry is not exactly identical with our idealized arrangement, we can expect the exchange integral to dominate. This is just a qualitative argument, but whatever the origin of ferromagnetic interstack coupling, it will be very weak. The dominant role has to be ascribed to the coupling within the stacks.

Finally a word to the mechanism discussed in this paper from a more general point of view. Here we restricted ourselves to $DMFc^+TCNE^-$, which was the first ferromagnetic material of this kind. In the meantime, there are several similar complexes that also exhibit ferromagnetic behavior.[15,16] It is of course desirable to examine the compatibility of our mechanism with these experimental results. This will be done in a subsequent paper. Here we just want to mention that the model is in line with the experimental observations for the compounds known so far so that a more general applicability of the spin polarization mechanism for this kind of compounds might be anticipated.

Acknowledgment. C.K. thanks the Deutsche Forschungsgemeinschaft for the award of a postdoctoral fellowship.

Appendix

Table II. Extended Hückel Parameters[a]

atom	orbital	H_{ii} (eV)	Slater exponent
C	2s	−21.4	1.625
	2p	−11.6	1.625
N	2s	−26.0	1.95
	2p	−13.6	1.95
H	1s	−13.6	1.3
Fe	3d	−11.9	5.35 (0.5577), 2.1 (0.60854)
	4s	−10.7	1.715
	4p	−6.32	1.15

[a] The coefficients for the double-ζ expansion of the Fe 3d orbitals are given in parentheses.

We performed an extended Hückel calculation for ferrocenium. The C–C and C–H bond lengths of the Cp rings are 1.41 and 1.09 Å, respectively. The distance between Fe and the planes of the Cp rings is 1.71 Å. A fragment molecular orbital (FMO) calculation[44] with Fe as one and the two Cp rings as the other fragment has been performed in order to break down the e_{1g} and $e_{1g}{}^*$ orbitals into the corresponding metal and Cp contributions.

In addition, another extended Hückel calculation was performed for a DMFcTCNE donor–acceptor pair. Again we used the FMO scheme with ferrocenium and the TCNE molecule as the two fragments. This allows us to find the overlap and resonance integrals between the π^* orbital of TCNE and the e_{1g} and $e_{1g}{}^*$ orbitals of ferrocenium. The C–C single and double bond lengths of TCNE are 1.42 and 1.39 Å, respectively. It should be noted

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(42) Izuoka, A.; Shigeru, M.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

(43) Maki, A. H.; Berry, T. E. *J. Am. Chem. Soc.* **1965**, *87*, 4437.

(44) (a) Hoffmann, R.; Fujimoto, H.; Swenson, J. R.; Wan, C.-C. *J. Am. Chem. Soc.* **1973**, *95*, 7644. (b) Hoffmann, R.; Fujimoto, H. *J. Chem. Phys.* **1974**, *78*, 1167.

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that the occupation of the π^* orbital shortens the single and lengthens the double bonds. The C–N triple bond length is 1.14 Å. We have chosen the symmetrical arrangement shown in Chart I (C_s symmetry). The planes of TCNE and the Cp rings are assumed to be parallel and separated by a distance of 3.51 Å. The resulting resonance and overlap integrals between the π^* orbital of TCNE and the e_{1g} and e_{1g}^* orbitals of ferrocenium are given in Table I. The integrals involving the orbitals b and b* vanish for symmetry reasons.

The H_{ii}'s and the Slater exponents of the extended Hückel calculation are given in Table II. The coefficients for the double-ζ expansion of the Fe d orbitals are given in parantheses.

Registry No. DMFcTCNE, 105399-77-7; ferrocenium, 12125-80-3.

Chemical Model Studies on the Mutagenesis of Benzofuran Dioxetanes in the Ames Test: Evidence for the Benzofuran Epoxide as Ultimate Mutagen

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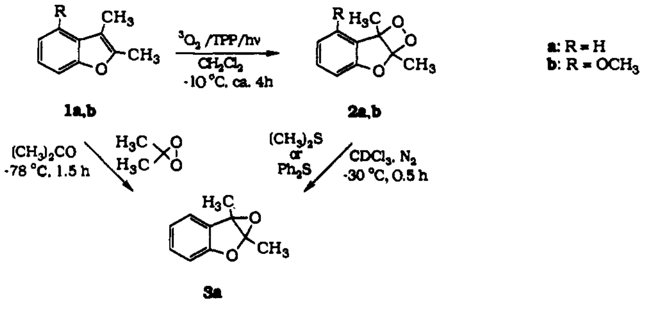
Abstract: The synthesis of the first benzofuran epoxide **3a** was achieved by epoxidation of the benzofuran **1a** with dimethyldioxirane and alternatively by deoxygenation of the benzofuran dioxetane **2a** with sulfides. This labile epoxide formed with nucleophiles such as water, methanol, thiophenol, and imidazole the corresponding adducts **13a–16a**. In contrast to epoxide **3a**, the dioxetanes **2** required acid catalysis (CF_3CO_2H) for the addition of water, methanol, and azide ion to give the corresponding adducts **9–11**; in the absence of nucleophiles the allylic hydroperoxides **8** were formed. The decomposition of benzofuran dioxetanes **2** in the polar, protic solvents water and methanol afforded not only the expected cleavage products **4** but also the 1,3-dioxols **5**, the spiroepoxide dimer **6a**, and the 1,4-dioxines **7**. An intramolecular electron-transfer mechanism is postulated for the formation of the spiroepoxide, which subsequently dimerizes to **6a** or rearranges into **5** and **7**. Only the benzofuran epoxide **3a**, besides the benzofuran dioxetanes **2**, was mutagenic in the *Salmonella typhimurium* strain TA100. Therefore, we implicate the epoxide **3a** as the ultimate mutagen responsible for the high mutagenic activity observed with dioxetane **2a** in the Ames test. We postulate that in the oxidative metabolism of polycyclic arenes and heteroarenes the corresponding epoxides are generated from the intermediary dioxetanes by deoxygenation with sulfides.

Extensive investigations on the photogenotoxicity of 1,2-dioxetanes—efficient sources of triplet excited carbonyl compounds—revealed that indeed DNA can be damaged when treated with dioxetanes under physiological conditions. For isolated calf thymus DNA pyrimidine dimers were detected[1] and for superhelical PM2 DNA pyrimidine dimer-specific repair endonucleases revealed a correspondence between the amount of dimer formation and the triplet excitation flux of alkyl-substituted dioxetanes.[2] Furthermore, additionally single strand breaks and apyrimidinic and apyrinic (AP) sites were observed, but these results suggest[1c,2,3] that such toxicological damage does not correspond to that caused by direct UV (260 nm) irradiation and appears to be more similar to that produced by singlet oxygen and radical species. In bacteria and mammalian cells the main damage was single strand breaks, which are presumably derived from active oxygen species.[1c,4] For example, in *Escherichia coli* bacteria, dioxetanes induce dose-dependent SOS function sfiA and in mammalian cells (HL-60, SHE) they generate micronuclei (damage at the chromosomal level).

Scheme I



It was, therefore, surprising that alkyl-substituted dioxetanes are not mutagenic in several *Salmonella typhimurium* strains (Ames test). Nevertheless, recently it was observed[2,5] that benzofuran dioxetanes **2** (Scheme I) are highly mutagenic in the *S. typhimurium* TA100 strain. Thus, these derivatives are the first known dioxetanes with potent mutagenicity. Since the mutagenic damage elicited by dioxetanes **2** in the *S. typhimurium* TA100 strain could not be photoreactivated,[2] the mutations seem not to be of typical photochemical origin such as pyrimidine dimers. Moreover, recent toxicological results imply[2] that an alkylating

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[1] (a) Lamola, A. A. *Photochem. Photobiol.* **1969**, *9*, 291. (b) Lamola, A. A. *Biochem. Biophys. Res. Commun.* **1971**, *43*, 893. (c) Adam, W.; Beinhauer, A.; Epe, B.; Fuchs, R.; Griesbeck, A.; Hauer, H.; Mützel, P.; Nassi, L.; Schiffmann, D.; Wild, D. In *Primary Changes and Control Factors in Carcinogenesis*; Friedberg, T., Oesch, R., Eds.; Deutscher Fachschriften-Verlag: Wiesbaden, 1986; p 64. (d) Lown, J. W.; Koganty, R. R.; Kopecky, K. R. *Photobiochem. Photobiophys.* **1986**, *12*, 295.

[2] (a) Adam, W.; Beinhauer, A.; Mosandl, T.; Saha-Möller, C. R.; Vargas, F.; Epe, B.; Müller, E.; Schiffmann, D.; Wild, D. *EHP, Environ. Health Perspect.* **1990**, *88*, 89. (b) Adam, W.; Hadjiarapoglou, L.; Mosandl, T.; Saha-Möller, C. R.; Wild, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 200.

[3] Epe, B.; Mützel, P.; Adam, W. *Chem.-Biol. Interact.* **1988**, *67*, 149.

[4] (a) Nassi, L.; Epe, B.; Schiffmann, D.; Adam, W.; Beinhauer, A.; Griesbeck, A. *Carcinogenesis* **1987**, *8*, 947. (b) Nassi, L.; Schiffmann, D.; Favre, A.; Adam, W.; Fuchs, R. *Mutat. Res.* **1988**, *198*, 53.

[5] (a) Adam, W.; Albrecht, O.; Feineis, E.; Reuther, I.; Saha-Möller, C. R.; Seufert-Baumbach, P.; Wild, D. *Liebigs Ann. Chem.* **1991**, 33. (b) Adam, W.; Hauer, H.; Mosandl, T.; Saha-Möller, C. R.; Wagner, W.; Wild, D. *Liebigs Ann. Chem.* **1990**, 1227.

0002-7863/91/1513-8005$02.50/0