^{1}H, ^{13}C, and ^{19}F Nuclear Polarizations in the Photochemistry of α,α,α-Trifluoroacetophenone

Peter J. Wagner* and Michael J. Thomas

Contribution from the Chemistry Department, Michigan State University, East Lansing, Michigan 48824.
Received November 19, 1979

Abstract: CIDNP effects are observed during irradiation of α,α,α-trifluoroacetophenone (TFA) and several of its ring-substituted derivatives. In cyclohexane, the major CIDNP involves disproportionation of $PhC(OH)CF_3$ radicals, although some ^{19}F emission (E) is also observed for regenerated TFA. In aromatic solvents containing acid, ^{19}F polarizations indicate protonation of the TFA-aromatic triplet exciplex to yield the $PhC(OH)CF_3$ aromatic radical-cation radical pair. In neutral acetonitrile containing good electron donors, the ^{19}F polarizations depend on both ketone and donor concentration. At [TFA] > 10^{-2} M, 1,4-dimethoxybenzene (DMB) gives no CIDNP when [DMB] < 10^{-2} M and enhanced absorption (A) when [DMB] > 10^{-2} M; Dabco gives E when [Dabco] < 10^{-2} M, A when [Dabco] > 0.05 M. Halogen substituents on either DMB or TFA do not alter the high-concentration A, which is quenched by the specific triplet quencher biphenyl. These results are interpreted as a rare example of a triplet mechanism polarization, in which rapid electron transfer to electron-spin polarized triplet TFA is followed by Overhauser cross-relaxation of the resulting electron-spin polarized ketyl radical and by rapid degenerate electron exchange with ground-state ketone. In acidified acetonitrile, DMB produces strong ^{1}H and ^{13}C multiplet polarizations, both A/E and E ^{19}F polarizations in regenerated TFA. These arise from $PhC(OH)CF_3/DMB^{+\cdot}$ pairs. The timing of protonation and the competition between net and multiplet effects are discussed.

Several years ago we decided to explore whether the relatively large hyperfine interactions of fluorine nuclei in organic radicals might combine with the low reduction potentials of fluorinated ketones to produce any unusual CIDNP effects in the photochemistry of α,α,α-trifluoroacetophenone (TFA). Heinz Roth of Bell Laboratories also began a similar investigation. Our independent work culminated in a communication in which our combined results were presented as evidence for a rare triplet mechanism for CIDNP.[1] Roth has since published a full account of his work.[2] In this paper we present the full details of our work, including a comparison of ^{1}H, ^{13}C, and ^{19}F CIDNP phenomena in the presence of acid.[3]

Our original study of the photochemistry of TFA[4] showed that UV irradiation produces triplet TFA quantitatively, intersystem crossing being 100% efficient. Like most triplet ketones, triplet TFA can interact with other molecules by four different basic processes: hydrogen-atom abstraction, exciplex formation, electron transfer, and electronic energy transfer. Photoreduction in cyclohexane presumably involves simple hydrogen atom abstraction.[4] Our previous studies[4-6] establish that the photoreduction of TFA by toluene and other alkylbenzenes proceeds via exciplex intermediates. We have assumed that triplet energy transfer to naphthalene and dienes occurs at the same nearly diffusion-controlled rate characteristic of other phenyl ketones.[7]

Electron transfer to triplet ketones is less common than CT quenching. Radical ions are observed only in polar solvents such as acetonitrile and only when electron transfer is exergonic.[8] The thermodynamics of excited-state electron transfer were first described by Weller:[9]

$$\Delta G = -E_{0,0} - E(A^-/A) + E(D/D^+) - T\Delta S - e^2/a\epsilon \quad (1)$$

The entropic and Coulombic terms in eq 1 are relatively constant and small compared to the excitation energy and the redox potentials of donor and acceptor.[10] Since the latter three are easily measured, ΔG values are easy to calculate.

CIDNP attributed to electron-transfer quenching of triplet benzophenones has been reported[11] but TFA had not been studied before this work. The reduction potential of TFA in acetonitrile is −1.43 V (corresponding to 32.9 kcal/mol) relative to SCE, as measured by cyclic voltammetry.[5] The triplet energy $E_{0,0}$ in polar solvents is 70.0 kcal/mol.[4] Therefore, for triplet-state electron transfer to be exergonic, the donor oxidation potential relative to SCE can be no greater than 32 kcal/mol. (This estimate allows +5 kcal for the last two terms in eq 1.[10]) Dabco (1,4-diazabicyclo[2.2.2]octane), $E(D/D^+)$ = 0.68 V (15.6 kcal/mol),[12] is a strong enough donor to reduce even nonfluorinated ketones.[11] In contrast, 1,4-dimethoxybenzene (DMB), $E(D/D^+)$ = 1.34 V (30.8 kcal/mol),[13] is a potential donor toward triplet TFA but not toward nonfluorinated ketones.

In our search for CIDNP phenomena involving TFA, we chose substrates most likely to interact with the triplet ketone by only one primary process. This report is separated into three sections corresponding to hydrogen-atom abstraction, electron transfer, and exciplex formation.

Experimental Section

Materials. α,α,α-Trifluoroacetophenone (TFA, Columbia) was distilled through a spinning-band column and was >99.9% pure by GLC. 1-Phenyltrifluoroethanol was prepared by $NaBH_4$ reduction of TFA. Substituted TFAs were prepared as described in the accompanying paper.[6] 1,4-Dimethoxybenzene and 1,4-diethoxybenzene were recrystallized from ethanol, then vacuum dried. Aldrich 1,2-dimethoxybenzene, 1,3-dimethoxybenzene, and 2-bromo-1,4-dimethoxybenzene were passed through alumina before use. 1,2,4-Trimethoxybenzene and anisole were distilled, and Dabco was sublimed before use.

Cyclohexane was purified by stirring over portions of sulfuric acid until the acid layer no longer became colored. After exhaustive washing with bicarbonate solution and water, the cyclohexane was dried with $MgSO_4$, then refluxed over and distilled from P_2O_5. Reagent-grade acetonitrile purified by the method of O'Donnell, Ayres, and Mann,[14] with a final distillation from anhydrous K_2CO_3, was used for ^{19}F and ^{13}C spectra. CD_3CN from Merck, Sharp and Dohme was used as received for ^{1}H spectra. Carbon tetrachloride was reagent grade and was used without purification or after distillation from K_2CO_3. Benzene and bromobenzene were purified as for cyclohexane.

Equipment. GLC analyses were carried out on a Varian 1200 GLC equipped with a flame ionization detector. The normal NMR and polarized NMR spectra were recorded on Varian Model A56/60D (^{1}H, ^{19}F) and Varian Model CFT-20 (^{13}C) NMR spectrometers. In recording the proton-decoupled ^{13}C spectra, generally 5000-8200 transients were collected with a pulse angle of ~20°, a sweep width of 4000-5000 Hz, a pulse width of 4 μs, a pulse delay of 0, and an acquisition time of 0.8-1.0 s.

Procedures. The samples were irradiated in the spectrometer probe using the method described by Tomkiewicz and Klein.[15] Light from a 1000-W high-pressure mercury-xenon lamp was focused through a 10-cm water filter and a 3-mm Pyrex plate, then reflected from a front surface mirror onto a quartz light pipe inserted into a Pyrex

0002-7863/80/1502-4173$01.00/0

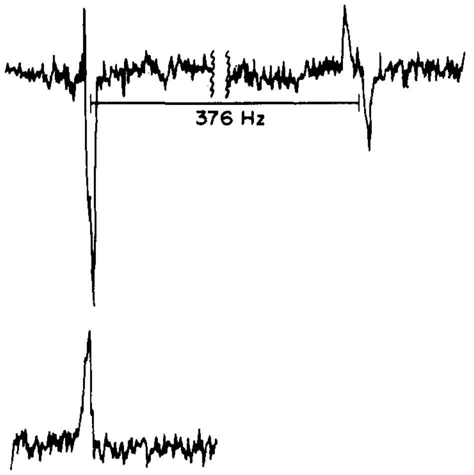
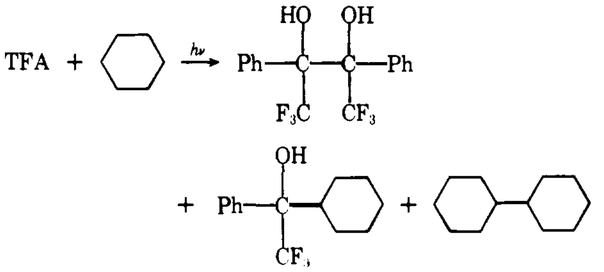


Figure 1. ^{19}F NMR spectra at δ 90.2 (CFCl$_3$) and upfield, 0.1 M TFA in cyclohexane. Top spectrum during irradiation, bottom one beforehand.

NMR tube. The depth of the light pipe in the tube and the position of the tube in the probe were adjusted to produce the strongest signals. Solutions were degassed by the freeze-pump-thaw method and then transferred in an inert atmosphere into the NMR tubes. The light pipe was inserted and held tight by an O-ring, which also served to keep air out of the tubes long enough for the experiments to be run.

Hydrogen Abstraction. Results

Cyclohexane was chosen as substrate/solvent. Normal radical coupling products are formed in low quantum efficiency.[4]



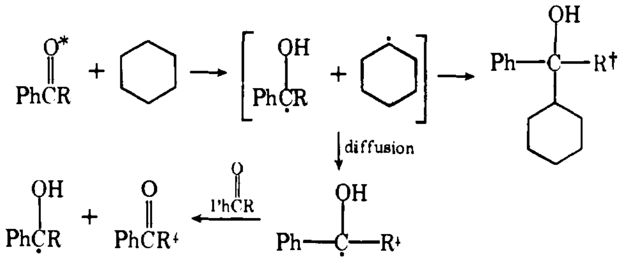
(2)

Irradiation in the NMR probe of degassed cyclohexane solutions 0.006-0.1 M in TFA initially produced an A/E multiplet for the fluorine triplet of TFA (δ 90.2 (CCl$_3$F), t, $^5J_{\mathrm{HF}}$(ortho) = 1.1 Hz). An A/E multiplet polarization corresponding to the fluorine doublet of the heretofore unreported 1-phenyl-2,2,2-trifluoroethanol ($^3J_{\mathrm{HF}}$ = 7.5 Hz) appeared 376 Hz upfield from the TFA signal. On continued irradiation a net emission (E) component developed in the TFA fluorine signal (Figure 1) and the ortho protons of TFA showed weak enhanced absorption (A). These net effects grew in more rapidly at the lower initial ketone concentrations. In the presence of 0.1 M BrCCl$_3$ or 0.2 M CCl$_4$ no multiplets appeared, only the TFA E remaining. Although substantial loss of ketone occurred during these irradiations, such that considerable concentrations of the cross-coupled product were formed, no ^{1}H or ^{19}F CIDNP could be observed for that cyclohexylcarbinol.

Hydrogen Abstraction. Discussion

Closs and Paulson briefly reported that irradiation of regular acetophenone in cyclohexane results in E polarization of the ketone methyl protons.[16] They suggested Scheme I which involves out-of-cage trapping of polarized α-hydroxy radicals by degenerate hydrogen transfer to ground-state ketone. The daggers † and ⸸ denote opposite nuclear polarizations.

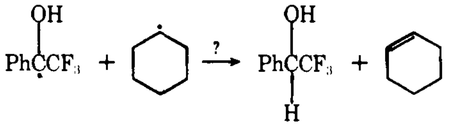
Scheme I



Such a scheme could conceivably explain the net effects observed with TFA. Kaptein's rules for net CIDNP effects predict A when Γ > 0, E when Γ < 0.[17] The photoreaction of TFA with cyclohexane is triplet derived[4] ($\mu > 0$); for nuclei on TFA $\Delta g > 0$ since $g(\mathrm{PhC(OH)CF_3}) \approx 2.0035$[2,3] and $g(\mathrm{C_6H_{11}}\cdot) \approx 2.0026$;[18] $a_{\beta\text{-F}} > 0$;[19] $a_{o\text{-H}} < 0$.[20] Therefore, if nuclear polarization arises from interaction between α-hydroxy and cyclohexyl radicals, ε must be negative.

$$\Gamma_{\mathrm{net}} = \Delta g a \mu \epsilon \qquad (3)$$

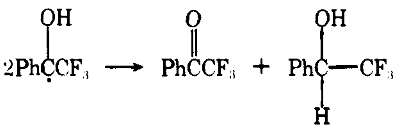
Two independent pieces of evidence do not fit with a Scheme I explanation for the polarizations observed with TFA. First, the scheme depends on the major in-cage radical-radical reaction *not* being one which regenerates ground-state ketone. If it were, out-of-cage polarization could decrease but never reverse the in-cage polarization.[1,2] The in-cage cross-coupling suggested by Scheme I does not result in observable CIDNP for that product, which would not be expected to have an unusually short nuclear relaxation time. An alternative cage reaction might involve disproportionation to yield alcohol plus cyclohexene. However, no CIDNP was observed for any protons, nor was any net polarization observed for the alcohol.



(4)

Another flaw with Scheme I is the time dependence of the observed net effects; they appear only after considerable photochemical reaction of TFA. Out-of-cage degenerate exchange of polarized α-hydroxy radicals with ground-state ketone should be most efficient at the beginning of irradiation, when ketone concentration is the highest; yet no net effect was observed then. In fact, net effects built up fastest at the lowest initial ketone concentrations. This buildup of net polarization strongly suggests that an in-cage process is responsible. Since cyclohexane is the only initial source of hydrogen, no radical pair with the proper Δg is available initially. However, the radical coupling products involving the PhC(OH)CF$_3$ radical are themselves alkylbenzenes, which are better quenchers of triplet TFA than is cyclohexane.[4] We suspect that the interaction of triplet TFA with one of these products produces a radical pair with Δg negative so that in-cage reversal can regenerate TFA with the observed net polarizations.

The multiplets seen for TFA and its dihydro product are readily accounted for by disproportionation of two α-hydroxy radicals. The signals are destroyed by added tetrahalomethanes which are efficient traps of α-hydroxy radicals.[21]



$$2\mathrm{Ph\dot{C}(OH)CF_3} \longrightarrow \mathrm{PhC(O)CF_3} + \mathrm{PhCH(OH)CF_3} \qquad (5)$$

Kaptein's rule for multiplets effects[17] indicates that A/E results from a negative product of six factors:

$$\Gamma_{\mathrm{mult}} = a_1 a_2 J_{12} \mu \epsilon \sigma \qquad (6)$$

For a pair of hydroxy radicals, $\mu > 0$ since the pair is produced

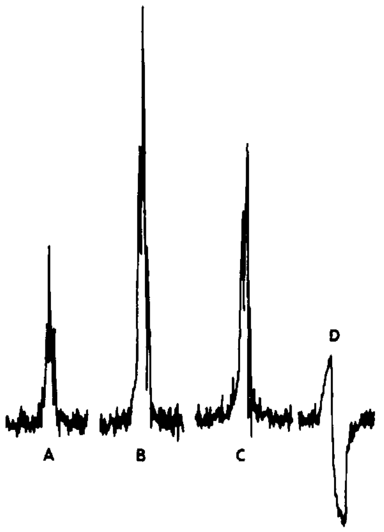


Figure 2. ^{19}F NMR signal at δ 90.2 ($CFCl_3$), 0.1 M TFA, 0.2 M DMB in acetonitrile: A, in dark; B, light on; C, light on, 0.3 M biphenyl present; D, light on, 0.05 M DMB, 0.25 M CCl_4 present.

by random encounters; $a_{\beta\text{-F}} > 0$ as discussed above; $\epsilon > 0$ since polarization involves regeneration of reactant. For the alcohol product, $\sigma < 0$ since the interacting nuclei start on different radicals; $a_{\mathrm{OH}} > 0$[22] and $^3J_{\mathrm{HF}} > 0$;[23] therefore, A/E is predicted. For the ketone, $\sigma > 0$ and $a_{o\text{-H}} < 0$;[20] the observed A/E pattern requires that $^5J_{\mathrm{HF}} > 0$. This latter assignment is uniquely consistent with our other results.

Electron Transfer Quenching. Results

Prolonged irradiation of degassed acetonitrile solutions containing TFA and either Dabco or DMB results in little, if any, net chemical reaction. No volatile products or TFA disappearance could be detected by GC analysis; no significant decreases in TFA signal intensities were observed after irradiation in any CIDNP experiments.

Irradiation of solutions held in NMR probes resulted in variable CIDNP phenomena depending on reactant concentrations and on solvent purity. As discussed in the next section, the presence of acid in the solvent produces strong CIDNP effects. In less than extensively purified acetonitrile, irradiation of TFA in the presence of several substituted benzenes including DMB produces weak ^{19}F E which fades during irradiation. In extensively purified acetonitrile, irradiation produces no CIDNP at 0.1 M TFA and at DMB concentrations below 0.005 M. At 0.02-0.2 M DMB, ^{19}F A was observed for the CF_3 signal of TFA when [TFA] $\geq 10^{-2}$ M; an A/E multiplet was observed when [TFA] $\leq 10^{-3}$ M.[1,2] Roth independently found that at 0.03 M TFA analogous ^{19}F A is observed when [DMB] $> 10^{-2}$ M and A/E when [DMB] $< 10^{-3}$ M.[2] The presence of 0.05-0.25 M CCl_4 changes the A observed for 0.09 M TFA/0.05 M DMB to an A/E multiplet with some E (Figure 2). In the high-concentration cases where ^{19}F A was observed, no ^{1}H or ^{13}C polarization of ketone signals could be observed, but the ^{1}H signals of both quenchers were severely broadened. At 0.1 M DMB and 0.1 M ketone, TFA as well as several of its ring-substituted derivatives including *p*-chloro-TFA all produced strong ^{19}F A (Figure 2). Likewise, 0.1 M TFA showed strong ^{19}F A when irradiated with 0.2 M of several other good donors including 1,4-diethoxybenzene, 1,2,4-trimethoxybenzene, and 2-bromo-1,4-dimethoxybenzene, weak A with 1,2- and 1,3-dimethoxybenzene, and no polarization with anisole. Inspection of the ^{1}H signals of the diethoxybenzene during irradiation showed severe broadening of the ring and CH_2 protons but no change at all in the CH_3 protons.

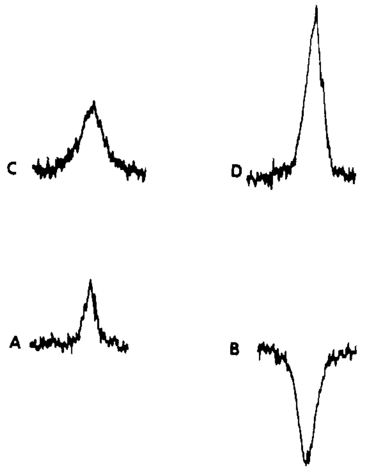


Figure 3. ^{19}F NMR signal at δ 90.2 ($CFCl_3$), 0.08 M TFA in acetonitrile containing various concentrations of Dabco: A, in dark; B-D, during irradiation with B, 10^{-3}-10^{-2} M, C, 0.05 M, D, 0.11 M Dabco.

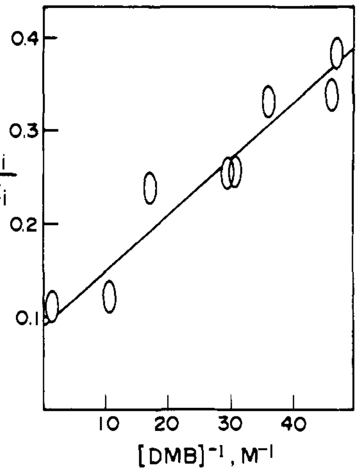


Figure 4. Double reciprocal plot of ^{19}F signal intensity (A) at δ 90.2 ($CFCl_3$) during irradiation of acetonitrile solutions containing 0.09 M TFA and various concentrations of DMB.

With Dabco as quencher, at [TFA] between 0.02 and 0.10 M, ^{19}F E was observed for the CF_3 of TFA when [Dabco] < 0.01 M and A when [Dabco] > 0.05 M (Figure 3).

The dependence of high concentration A intensity on donor concentration was studied carefully for DMB and found to increase in the range 0.02-0.50 M. Figure 4 is a typical double reciprocal plot[24] of inverse A intensity vs. inverse [DMB]. I is the steady-state ^{19}F signal intensity during irradiation; I_i is the intensity before (or after) irradiation; α is a product of several experimental and instrumental constants; τ' is the lifetime of the excited species being quenched; k_q is the rate constant for quenching by DMB. The latter is known to equal $1.2 \times 10^{10}\ M^{-1}\ s^{-1}$ for triplet TFA.[6] The intercept/slope of the plot equals $k_q\tau'$ and has a value of 15 M^{-1}. If triplet quenching is involved, $\tau' = 1.2$ ns.

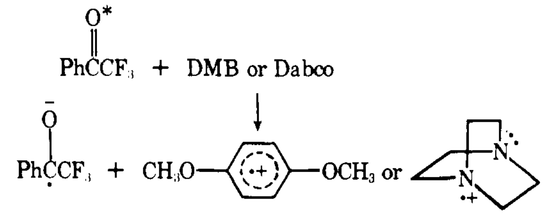
$$I_i/(I - I_i) = \alpha + \alpha(k_q\tau'[\mathrm{DMB}])^{-1} \qquad (7)$$

Two separate experiments were performed to establish whether the high concentration A seen with both DMB and Dabco represents singlet or triplet ketone quenching. In the first, acetonitrile solutions containing 1 M *cis*-1,3-pentadiene and 0.08 M TFA were irradiated in the presence of 0.046 M DMB or 0.09 M Dabco. The former lowered the quantum efficiency of sensitized cis-trans diene isomerization to 96%, the latter to 93%, that observed in parallel blank solutions with no electron donor quenchers present. Both small decreases are quantitatively what would be expected if the added donors acted only as competitive triplet quenchers (with the same diffusion-controlled quenching rate constant for diene and both donors). Any significant singlet quenching would have lowered the sensitized isomerization efficiencies even more.

In a second experiment the effect of added biphenyl on TFA CIDNP was ascertained. Biphenyl quenches triplet phenyl ketones[25] but not excited singlet ketones.[26] The biphenyl quenches both the A and E seen at various concentrations of Dabco as well as the high concentration DMB A (Figure 2).

Electron Transfer Quenching. Discussion

Observation of ^{19}F nuclear polarization in TFA indicates that excited TFA reacts with DMB and with Dabco to provide radical species which revert to ground-state TFA. The absence of labile hydrogens in the two donors and the lack of radical coupling products combine with the thermodynamic considerations presented in the Introduction to suggest that the observed effects arise from revertible[27] electron transfer. The observed broadening of donor proton signals, presumably because of degenerate electron exchange, is common to photochemical electron-transfer processes.[11] The total lack of any polarization in the methyl signals of diethoxybenzene suggests that revertible hydrogen atom abstraction is not even a minor contributor to the observed polarizations. The inability of anisole, with its high oxidation potential (1.76 eV),[13] and the weak ability of the other dimethoxybenzenes ($E_{ox} > 1.4$ eV)[13] to promote TFA CIDNP provide further evidence for an electron-transfer process.



Low-Concentration Quenching. The CIDNP effects seen at low donor concentrations are readily explained by the radical-pair theory.[30] DMB[6] and Dabco[31] both quench triplet TFA, which has a lifetime near 1 μs in acetonitrile, with a bimolecular rate constant $\geq 10^{10}$ M^{-1} s^{-1}. Therefore quencher concentrations above 10^{-4} M quench over half the ketone triplets and should produce radical ions efficiently. The g value for TFA radical anion (TFA$^{-}\cdot$) is 2.003 75;[32] that for DMB radical cation (DMB$^{+}\cdot$) is 2.003 68;[33] and that for Dabco$^{+}\cdot$ is 2.0040.[32] The TFA$^{-}\cdot$, DMB$^{+}\cdot$ radical pair has a Δg value very close to zero, so that multiplet polarization should be dominant. Since $\epsilon > 0$ for systems involving only regeneration of reactants,[2] the A/E pattern observed by Roth[1,2] is predicted by eq 6, as explained above, if $^5J_{HF} > 0$. With Dabco, net emission is predicted by eq 3, since Δg is negative.

It is noteworthy that these radical-pair polarizations were relatively weak, presumably because degenerate electron exchange with ground-state ketone is so rapid ($k > 10^8$ M^{-1} s^{-1})[34] that polarized ketyl radicals which escape the initial geminate cage nearly cancel in-cage polarization. This conclusion is a further statement that ϵ must be positive in such processes. Roth has verified this phenomenon in the effect of ground-state ketone concentration on such CIDNP.[2]

High-Concentration Quenching. The radical-pair theory of CIDNP cannot explain the nuclear polarizations seen at high donor concentrations for several reasons. The shift from E to A for Dabco might be interpreted as a shift from triplet to singlet ketone quenching.[16,28] However, the sensitization and especially the biphenyl quenching experiments indicate that the A observed for both donors involves only triplet TFA. The change from multiplet to net effect with DMB would demand different chemical mechanisms at different DMB concentrations, a situation without precedent. Even such an unlikely explanation is unsatisfactory because the A observed with TFA/DMB is independent of Δg; it appears equally strongly for TFA/2-BrDMB and for p-ClTFA/DMB. Any conceivable radical pairs produced from these latter two systems should have Δg values of opposite signs and therefore should produce opposite polarizations if the simple radical-pair mechanism were operating.[35]

There are two more observations outside the domain of Kaptein's rules which do not fit a radical-pair mechanism. As discussed above and below, ^{1}H polarizations are readily observable in other photoreactions of TFA. The observation of only ^{19}F polarization in these neutral solutions is thus unusual.

Finally, the τ' value of 1.2 ns is only $^1/_{1000}$ the measured lifetime for thermally equilibrated TFA triplets.[6] The value is, however, in the range suggested for electron spin polarized triplets;[36] therefore a mechanism involving such a species must be considered.

The triplet mechanism for CIDNP consists of the key steps summarized in Scheme II.[29] In this scheme * denotes electronic excitation, ‡ electron-spin polarization, and † nuclear spin polarization. The mechanism involves, chronologically, (1) nonequilibrium population of triplet sublevels during intersystem crossing; (2) transfer of this electron spin polarization to radical products during chemical reaction; (3) Overhauser electron–nuclear cross-relaxation; (4) degenerate exchange of the resulting nuclear polarized radical with ground state to produce a nuclear polarized ground-state molecule.

Scheme II

$$^1\mathrm{TFA}^{*} \rightarrow {}^3\mathrm{TFA}^{\ddagger *} \quad (8)$$

$$^3\mathrm{TFA}^{\ddagger *} + \mathrm{D}: \rightarrow {}^{\ddagger}\mathrm{TFA}^{-}\cdot + \mathrm{D}^{+}\cdot \quad (9)$$

$$^{\ddagger}\mathrm{TFA}^{-}\cdot \rightarrow {}^{\dagger}\mathrm{TFA}^{-}\cdot \quad (10)$$

$$^{\dagger}\mathrm{TFA}^{-}\cdot + \mathrm{TFA} \rightarrow {}^{\dagger}\mathrm{TFA} + \mathrm{TFA}^{-}\cdot \quad (11)$$

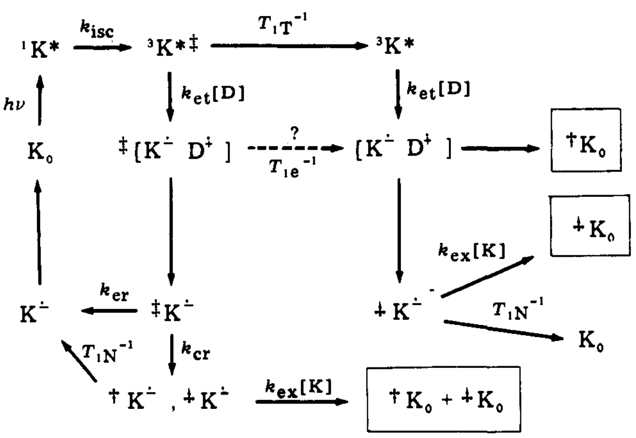
This mechanism can be appraised on three levels: its general feasibility, its feasibility for TFA, and its quantitative aspects.

The observation of EPR emission during various bimolecular photoreactions of carbonyl compounds[37] (CIDEP) establishes that there is some path for formation of electron-spin polarized radicals. The first two steps in Scheme II comprise the triplet mechanism postulated for such CIDEP observations.[38] A key feature is that step 2 be fast enough that it can compete with rapid spin–lattice relaxation of the triplet sublevels. Our observed donor concentration effect is identical with that observed for amines in their ability to promote quinone CIDEP.[36] Our explanation of concentration-dependent CIDNP depends not so much on the correctness of the details of the triplet mechanism for CIDEP as it does on the experimental observation of analogous concentration-dependent spin polarized radical formation.

The original suggestions of spin-polarized triplets and Overhauser effects being responsible for CIDNP[39] were rejected by Closs because, among other reasons, the substrates then being considered reacted too slowly with triplet ketones to possibly trap a spin-polarized triplet.[40] Nonetheless, intersystem crossing of molecules with any symmetry affords spin-polarized triplets;[41] any diffusion-controlled bimolecular reaction of such triplets should be able to trap at least some of the electron spin polarization. This rapid-quenching requirement certainly is met in our system. In fact, these crucial substrate concentration effects have not been reported for other systems thought to show triplet CIDNP.

Given the known formation of electron-spin polarized radicals, the crucial additional steps for the observation of CIDNP are cross-relaxation and exchange with ground-state molecules.

Scheme III



These two processes must compete with electron and nuclear spin relaxations, respectively. Moreover, any CIDNP produced by this four-step mechanism must compete with possibly offsetting CIDNP produced by the normal radical-pair mechanism. Adrian and Wan have already considered steps 3 and 4.[29] The probability of cross-relaxation producing a polarized nuclear spin distribution of any given atom in a radical is proportional to the square of the hyperfine interaction of that atom's nuclear spin with the molecule's electron spin.[29,42] Therefore CIDNP is likely only for nuclei with large hyperfine coupling constants, such as fluorine.[43] Even when there is high probability for cross relaxation, the nuclear spin polarized radicals so formed must be returned to stable ground-state reactant before they undergo too much nuclear spin relaxation. Such a process requires a rapid bimolecular exchange reaction; its probability thus depends on the concentration of the appropriate ground-state species. Adrian and Wan's experimental evidence for triplet mechanism CIDNP in fact involved the effect on the CIDNP intensity of benzoquinone of ground-state quinone concentration.[29]

The Triplet Mechanism for TFA. Electron transfer to TFA has all of the characteristics required for successful observation of triplet mechanism CIDNP. In all phenyl ketones studied, intersystem crossing preferentially populates the higher energy triplet sublevels, both at zero field[44] and at high magnetic field.[45] As described above, electron transfer from DMB and Dabco is diffusion controlled such that high concentrations of donors can intercept the spin-polarized triplets within their ~1-ns lifetime. Although no CIDEP experiments have been reported for TFA,[46] it seems highly probable that the TFA$^-\cdot$ ketyls produced by rapid electron transfer exist in a nonequilibrium distribution of electron spin states, probably favoring the higher energy one. The fluorine atoms in TFA$^-\cdot$ exhibit large hyperfine splittings,[32,47] such that cross-relaxation should be efficient. The absence of ^{1}H polarization accompanying the ^{19}F A is uniquely explained by a cross-relaxation mechanism. Finally, degenerate electron exchange between ketones and their ketyl radical anions is very rapid, bimolecular rate constants of 10^8 M^{-1} s^{-1} for several ketones[34] having been measured. Therefore reasonable concentrations of ground-state ketone would allow step 4 of Scheme II to compete very well with nuclear spin relaxation of the ketyl radicals, since typical radical T_{1N}^{-1} values are lower than 10^6 s^{-1}.[48] Just as important, this rapid exchange minimizes the importance of any competing radical pair CIDNP for the reasons outlined above and detailed so elegantly by Roth.[2] Scheme III presents all the mechanistically important reactions for nuclear polarizations due to revertible electron transfer, with K standing for TFA or any other acceptor. The † and ↓ denote opposite nuclear polarizations.

The complexity of Scheme III partially explains why triplet mechanism CIDNP is not common; it demands the rare coincidence that five different stringent kinetic requirements all be met. Even 1 M donor can trap no more than 90% of the spin-polarized triplets. It is uncertain how much spin relaxation occurs before diffusion apart of the electron spin polarized radical ion pair. T_{1c} for the pair must fluctuate because of diffusive motions with a value somewhere between the 10^{-9} s for the triplet and the 10^{-6} s common for doublets. Since zero-field spin-spin interaction in radical pairs is quite weak,[49] it is likely that T_{1e} approaches the longer limit. With a geminate pair lifetime on the order of 10^{-8} s,[30] it is quite probable that no more than 10% of the polarized radical pairs relax before diffusing apart. Nonetheless, potential radical-pair CIDNP can always compete with that produced by the triplet mechanism. Our observation of A at lower concentrations of DMB than of Dabco is probably explained by the lack of any net radical pair effect with DMB, so that the polarization produced by the triplet mechanism could not be masked by any opposite radical pair polarization. With Dabco, over 80% of the spin polarized triplet TFA must be trapped before the triplet mechanism A is no longer offset by radical pair E.

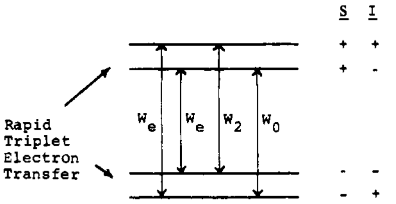


Figure 5. Competing electron spin relaxation processes of spin polarized radicals formed by rapid triplet quenching.

Efficiency and Direction of Cross-Relaxation. What remains to be discussed is the nature of the cross-relaxation step in TFA$^-\cdot$. Figure 5, adapted from Adrian,[29] describes the various spin relaxation processes which can occur in an electron spin polarized radical.

W_e describes the rate of pure electron spin relaxation, while W_2 and W_0 describe rates of cross-relaxation. There are two important quantitative questions regarding our results. Cross-relaxation can produce nuclear polarization in both senses, as noted in Scheme III, depending on the relative values of W_2 and W_0. For the triplet mechanism to be responsible, A can arise only if $W_0 > W_2$ in TFA.[2] Second, the relative values of $(W_0 - W_2)$ and W_e partially determine the probability that nuclear polarization will arise from rapid triplet quenching and thus the size of the "enhancement factor" or CIDNP intensity. The other main determinant of this probability is the actual polarization established during intersystem crossing.

$$(W_2 - W_0)^{\text{dipole}} = \frac{B_{zz}^2\tau_R}{8h^2(1 + \omega_Z^2\tau_R^2)} \tag{12}$$

$$W_0^{\text{scalar}} = \frac{\delta A^2\tau_A}{2h^2(1 + \omega_Z^2\tau_A^2)} \tag{13}$$

$$W_e' = \frac{3B_{zz}^2\tau_R}{80h^2(1 + \omega_Z^2\tau_R^2)} \tag{14}$$

$$1/T_{1e} = k_{er} + k_{cr} \tag{15}$$

Both questions can be evaluated by estimating the values of the various relaxation rates. Cross-relaxation is promoted primarily by hyperfine interactions. Since W_2 measures a process with a net change of total spin, a dipole mechanism is necessary and is provided by modulation of the anisotropic components of the hyperfine interaction. The dipole mechanism also provides a component to W_0, but one equal to only about $\frac{1}{6}W_2$.[29] Equation 12 describes the overall rate of cross-relaxation which would be expected to preferentially populate the *higher* energy nuclear spin state; B_{zz} is one component of the anisotropic hyperfine splitting tensor, ω_Z is the electron precession frequency (Zeeman splitting), and τ_R

is the rotational correlation time of the radical (since molecular tumbling modulates the anisotropic hyperfine interactions). W_0 also has a scalar component provided by modulation of the isotropic hyperfine interactions. Equation 13 describes the rate of this process, with A equaling the isotropic hyperfine splitting and τ_A the correlation time of the CF_3 rotation. Equation 14 defines that portion of W_e which is determined by hyperfine interactions. Note that k_{er} would be only 60% as large as k_{cr} if no other mechanism contributed significantly to the value of W_e.

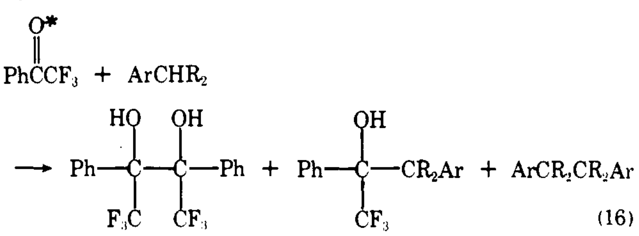
Strictly speaking, the above equations apply to radicals with axially symmetric hyperfine interactions; their use for TFA represents the best available estimates of relaxation rates. Since $TFA^{-}\cdot$ is not spherical, there are different values for τ_R describing tumbling about the three axes which correspond to the principal directions of the anisotropic hyperfine tensors. For simplicity we can consider TFA and its ketyl as cylinders with 6-Å diameter and 10-Å length. The only measured anisotropic hyperfine splittings for β fluorines on a CF_3 group are for the $CF_3CFCONH_2$ radical,[50] for which B values of 101, 48, and 39 MHz were measured. The largest component lies along the CF_3-CF C-C bond.[50,51] For simplicity we will assume comparable B values and principal axes in $TFA^{-}\cdot$. We then find that the tumbling motions which modulate the largest hyperfine splitting require rotation of the molecule's longest axis and thus have the longest τ_R. With $\omega_Z = 4 \times 10^{10}$ Hz[52] and $\tau_R \approx 1.0 \times 10^{-10}$ s,[53] eq 12 predicts a cross-relaxation rate on the order of 1×10^4 s^{-1} from modulation of the largest hyperfine component. Equation 13 indicates that W_0 scalar exceeds 1×10^4 s^{-1} only when the rotational correlation time for the CF_3 group is shorter than 0.2 ns. Such rotational rates are usually in the range of 10^{10}-10^{11} s^{-1}; a rate corresponding to ω_Z would give the maximum value of $W_0 = 3.5 \times 10^4$ s^{-1}.

We reemphasize the approximate nature of the above estimates. Nonetheless, what quantitative calculations are possible indicate that in the case of TFA it is not unreasonable for scalar cross-relaxation to predominate over the dipolar mechanism and thus produce the observed overpopulation of the lower energy nuclear spin state. Roth has provided splendid independent evidence by observing ^{19}F emission from meta and para fluorines on TFA;[2] their hyperfine interaction with the unpaired spin density on the ketyl radical can be modulated only by molecular tumbling.[29]

Our final concern is with the extent of nuclear polarization produced by this triplet mechanism. The other main mechanism for electron spin relaxation besides hyperfine interactions is g-factor anisotropy.[29,42] The magnitude of the anisotropy for $TFA^{-}\cdot$ is unknown. If we assume a $g_{\parallel} - g_{\perp}$ value of 0.004 (as in tetrafluorobenzoquinone,[29] vs. only 0.002 in $^{-}O_2CCF_2CFCO_2^{-}$ [19]), we calculate[29] a total k_{er} on the same order as k_{cr}, which is approximately 5×10^4 s^{-1}. T_{1e} values for radicals are normally in the 10^{-5}-10^{-6} s range. Therefore we tentatively conclude that cross-relaxation is somewhere between 5 and 50% efficient at causing nuclear polarization. We do not know the degree of polarization involved in formation of $TFA^{-}\cdot$. The A observed at higher quencher concentrations is at least ten times more intense than the ground-state absorption, but we do not know what fraction of the ground-state ketones are excited per unit time and therefore cannot calculate a quantum efficiency for nuclear polarization. However, if the initial overpopulation of the radical's upper electron spin state is only 0.01% and 10% of these radicals undergo cross-relaxation via the scalar mechanism, each reformed ground state TFA would show NMR absorption some 30 times more intense than that of unexcited ground state.

Exciplex Quenching. Results

Whereas triplet TFA is quenched by benzene and all of its substituted derivatives so far studied,[4,6] it undergoes efficient photoreduction only when the aromatic contains benzylic hydrogens.[4,5] Net ^{19}F polarizations could be observed upon



$$PhC(=O^{*})CF_3 + ArCHR_2 \rightarrow Ph-C(OH)(CF_3)-C(OH)(CF_3)-Ph + Ph-C(OH)(CF_3)-CR_2Ar + ArCR_2CR_2Ar \quad (16)$$

irradiation of degassed acetonitrile solutions containing TFA and any of several substituted toluenes: weak A for xylene and toluene, strong E for p-bromotoluene. These effects could indicate some in-charge disproportionation of the α-hydroxy and benzyl radicals which lead to the observed radical coupling products. However, no ^{19}F or ^{1}H CIDNP could be observed for any of the coupling products in behavior reminiscent of that observed with cyclohexane as the solvent.

These product-forming reactions were not studied further when it was discovered that CIDNP effects are also observed under conditions where no radical coupling products are formed. For example, in neat benzene or in acetonitrile solutions containing benzene, anisole, or bromobenzene, ^{19}F E from TFA could be observed. However, polarization intensities were highly variable, depending on solvent purity, and often disappeared upon continued irradiation. In acetonitrile which had been carefully treated to remove acidic impurities, the light-induced polarizations were minimal or altogether absent. It was then found that the addition of various acids to the solutions resulted in very strong CIDNP effects. We then decided to study specifically this apparent acid-catalyzed CIDNP.

Irradiation of 0.09 M TFA in benzene containing 0.1 M acetic acid produces weak ^{19}F E, which fades with continued irradiation, at the chemical shift corresponding to TFA. However, the presence of 0.1 M trifluoroacetic acid produces a stable steady-state A/E multiplet. A comparable solution in C_6D_6 shows A/E multiplet polarization for the ortho protons of TFA. TFA (0.09 M) in anisole containing 0.2 M CF_3COOH shows ^{19}F E superimposed on the A/E multiplet. Irradiation of comparable solutions in bromo- and chlorobenzene gives very strong ^{19}F E. Figure 6 depicts these results.

A more thorough study was made of the effects of acid on the CIDNP observed upon irradiation of acetonitrile solutions containing DMB and various substituted TFAs. In all cases strong polarizations were noted for all the nuclei (^{1}H, ^{13}C, and ^{19}F) of TFA when either 0.1 M acetic acid or 0.005 M p-toluenesulfonic acid were present. The ^{19}F and ^{1}H signals observed with TFA and its p-chloro derivative (p-ClTFA) are exactly the same in the presence of either 0.0014 or 0.1 M DMB. In all cases signal intensities after irradiation were unchanged from those before irradiation; little if any net photochemical destruction of ketone occurred during these NMR experiments. In some cases, multiplet effects are superimposed upon net ^{19}F emission. Table I summarizes the polarizations observed. Figure 7 shows the ^{19}F signals observed for some of the ketones. Figure 8 shows some ^{1}H CIDNP for TFA protons plus substantial broadening of the aromatic protons of DMB. Figure 9 shows ^{13}C spectra for p-ClTFA.

Exciplex Quenching. Discussion

Aromatic solvents, as indicated in the Introduction, should form exciplexes with triplet AF_3 very efficiently. However, complete one-electron transfer from benzene, anisole, chlorobenzene, or bromobenzene to triplet TFA is too endothermic to occur with any significant efficiency. Therefore the strong, steady-state CIDNP effects observed for such solutions only when strong acid is present must be due to some specifically

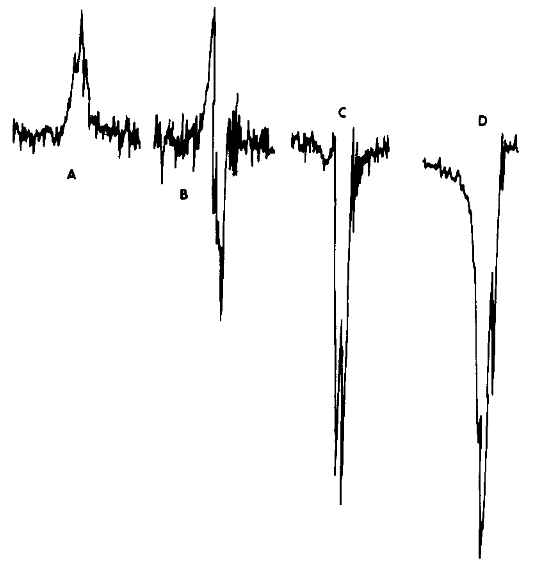


Figure 6. ^{19}F NMR signals at δ 90.2 ($CFCl_3$) for 0.09 M TFA and 0.1 M trifluoroacetic acid in B, benzene; C, anisole; D, bromobenzene (×¼), all during irradiation; A, before and after irradiation.

Table I. Summary of Nuclear Polarizations Observed[a] during Irradiation of Substituted TFAs in Acetonitrile Containing 0.05 M DMB and 0.1-0.3 M Acetic Acid

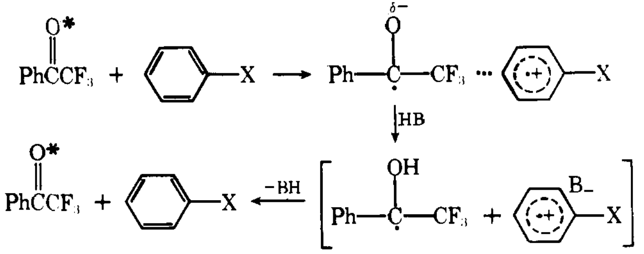
substituent	^{19}F	^{1}H (ortho)	^{1}H (meta)	$^{13}C{=}O$	$^{13}CF_3$
none	E + A/E′	A/E	*b*	E/A + E′	E/A
p-Cl	A/E	A/E	E/A	E/A	E/A
p-CH_3	E + A/E′	A/E	E/A		
p-OCH_3	E + A/E	A/E	E/A	E + E/A	E/A
m-CF_3	E + A/E′	A/E			

[a] A prime indicates a weak polarization. [b] The multiplet consisting of the meta and para protons has the upfield signals in A and the downfield signals in E.

acid-catalyzed radical-*formation* process. It has already been reported that TFA undergoes a concomitant acid-catalyzed photoreduction in benzene.[54] (Our present results suggest that this unusual photoreaction proceeds in very low quantum yield.) Apparently the exciplexes which are known to be formed do not proceed to radicals (no products or CIDNP) unless they are protonated. There is other evidence that the ketone half of triplet exciplexes must be protonated for net chemistry to ensue.[55] Since the CIDNP which we have observed involves only unchanged reactant TFA, we presume that nuclear polarization involves in-cage oxidation of protonated ketyl by aromatic radical cations.

The strong E seen with the halobenzenes supports the simplicity of Scheme IV, since Δg would certainly be negative while a_F, μ, and ϵ are all positive. However, the pure multiplet seen with benzene and the mixed polarizations seen with anisole require more elaborate explanation. Protonation of ketyl radical anions lowers their g values by 0.0002-0.0003.[56] Therefore the g of $PhC(OH)CF_3$ most probably has a value very close to 2.003 50.[3] The g value for benzene radical cation is only 2.0024.[57] Therefore the large positive Δg should produce strong A. The g value for anisole radical cation must be intermediate between those of benzene and DMB (~2.0030), so that a multiplet effect might be observable, but one superimposed on A, not E.

Scheme IV



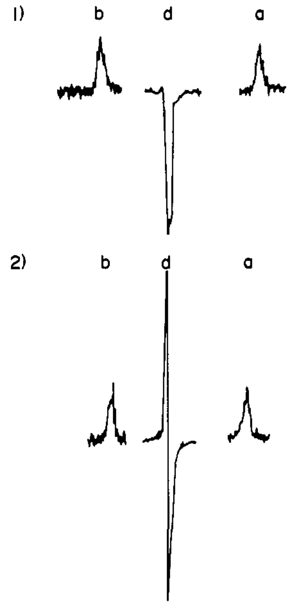


Figure 7. ^{19}F NMR signal at δ 90.2 ($CFCl_3$) of acetonitrile solution containing 0.1 M DMB, 10^{-2} M *p*-toluenesulfonic acid, and (1) 0.1 M TFA or (2) 0.1 M *p*-ClTFA. b, d, and a denote before, during and after irradiation; 2.5-fold decrease in spectrum amplitude during irradiation.

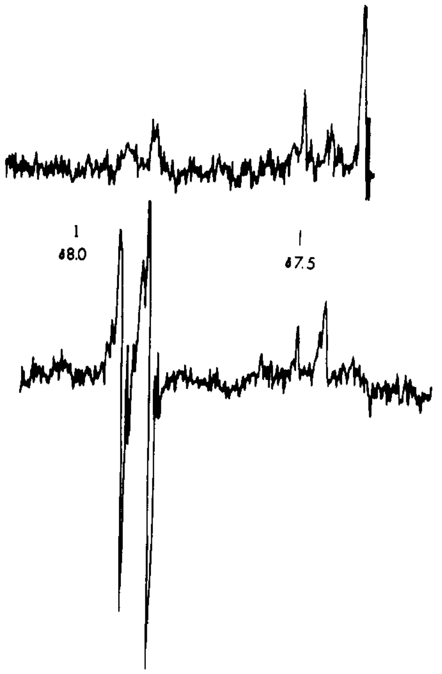


Figure 8. ^{1}H NMR spectra of 0.09 M *p*-ClTFA, 0.05 M DMB in acetonitrile-d_3 containing 0.02 M acetic acid: top, before irradiation; bottom, during irradiation.

Disproportionation of two hydroxy radicals might explain the A/E multiplets, as explained for the behavior of TFA in cyclohexane, except that no ^{19}F polarization could be found for the corresponding alcohol. It does not seem likely that the nuclear relaxation times of ^{19}F in the alcohol would be so much shorter in benzene than in cyclohexane that no steady-state polarization would be observable. Since the change from

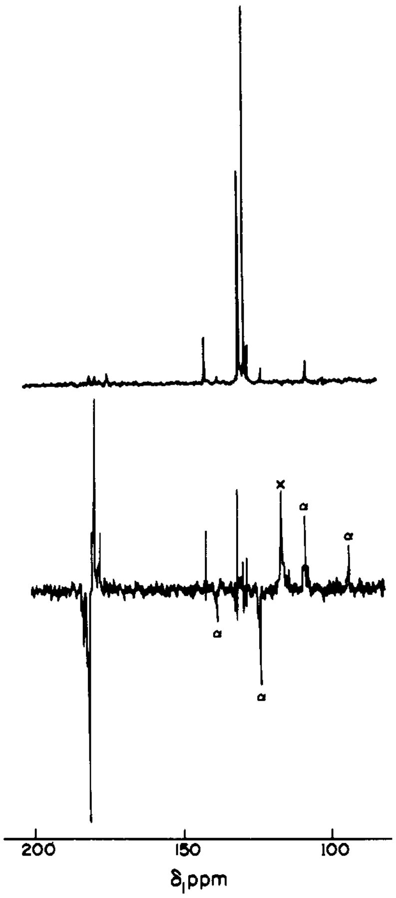


Figure 9. Proton-decoupled FT ^{13}C NMR spectra of *p*-ClTFA in acetonitrile: top, 1 M ketone after 8200 pulses in the dark; bottom, 0.1 M ketone, 0.065 M DMB, and 0.2 M acetic acid after 5000 pulses during continuous irradiation. Peaks marked α represent CF_3 quartet; x marks a solvent peak.

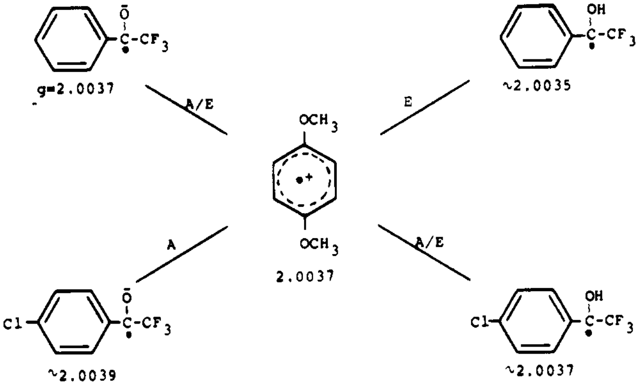
multiplet to mixed to pure net effects parallels the increasing *g* values of the donor-derived radical cations but not donor electron-donating abilities, it is more likely that the observed change in polarization type reflects changes in S ↔ T rates in radical pairs rather than in overall gross chemistry.

Given the low ion-solvating ability of aromatic solvents, any aromatic radical cation and conjugate base B^- such as pictured in Scheme IV would exist as very tight ion pairs. Even in good cation-solvating solvents, metal ketyls such as sodium benzophenone exhibit hyperfine splitting by the metal ions.[58] If the same partial shift of spin density from radical ion to counterions occurs in our system, there should be enhanced spin-orbit coupling (more free spin on oxygen in B^-) and therefore increased *g* values. What we are suggesting is that ion pairing causes the benzene$^{+}\cdot$, RCO_2^- ion pair to have a *g* value slightly below 2.0035 and the anisole$^{+}\cdot$, RCO_2^- pair one slightly above 2.0035.

DMB in Acetonitrile. As discussed above, complete electron transfer to yield radical ions can occur. It is likely that an exciplex is first formed and then normally decays very rapidly to ions.[59] As discussed above, protonation of the carbonyl oxygen at some stage must be responsible for the acid-catalyzed CIDNP. We shall first interpret the observed CIDNP in terms of $PhC(OH)CF_3$ radicals and then discuss when protonation occurs.

^{19}F. The key observation is the difference in polarizations observed for TFA (E + A/E) and *p*-ClTFA (only A/E). Scheme V compares the opposite effects of para chlorination[60] and of protonation on radical *g* values and on the ^{19}F polarization expected for the four possible radical pairs with DMB$^{+}\cdot$. As discussed above, back electron transfer in a ketyl$^{-}\cdot$, DMB$^{+}\cdot$ radical pair should give A/E for TFA ($\Delta g \approx 0$) and A for *p*-ClTFA ($\Delta g > 0$). (μ, ϵ, $a_{B\text{-}F}$, σ, and $^5J_{HF}$ are all positive; $a_{o\text{-}H}$ is negative.) In fact such polarizations can be seen only in the absence of acid and at low reactant concentrations. The polarizations observed in the presence of acid clearly are what would be expected for a protonated ketyl, DMB$^{+}\cdot$ radical pair. The mixed polarization observed for *p*-MeOTFA is consistent with an intermediate *g* value for its ketyl. We presume that in acetonitrile ion pairing is not so tight that the conjugate base of the added acid can affect the DMB$^{+}\cdot$ *g* value.

Scheme V



The actual process which generates nuclear polarized ketone most likely is oxidation of the protonated ketyl by DMB$^{+}\cdot$. Given the relatively high ketone concentration employed, one must ask why the observed polarizations are so strong, i.e., why rapid degenerate exchange of cage-escape radicals does not largely offset in-cage polarization. Roth[2] has addressed this very point by noting that degenerate H-atom exchange between protonated ketyls and ground-state ketones is slower than degenerate electron exchange involving ketyl radical anions, so that polarized escape radicals undergo substantial spin-lattice relaxation before being trapped.

^1H Polarizations. The strong A/E polarization of the quartet fluorine splitting of the ortho-proton signal in all TFAs studied corresponds to the A/E polarization of the ortho-hydrogen splitting of the ^{19}F resonances in most of the TFAs studied. The meta-proton signals, however, all show E/A polarization of the fluorine splittings. These multiplets are very weak and deserve mention only because they do not fit the pattern predicted by Kaptein's rules. However, these rules apply only to first-order nuclear couplings. In systems exhibiting second-order coupling effects, such as aromatic protons, "second-order" multiplet effects are possible[30b] and may be occurring here.

^{13}C polarizations have been reported in only a few systems. The strong signals we see for the carbonyl and CF_3 carbons, both E/A quartets because of coupling to the three fluorines, represent tremendous enhancement factors. Note that full-scale signals were accumulated after only half the pulses needed to barely see either carbon resonance in the 1 M dark solution. The E/A multiplet patterns are expected since σ, μ, ϵ, and a_F are all positive; for $C = 0$, $^2J_{CF}$[61] and a_C[62] are both positive; for CF_3, $^1J_{CF}$[61] and a_C[63] are both negative.

The carbonyl ^{13}C polarization takes on a strong E component in *p*-methyl- and methoxy-TFA. It is not apparent to what magnetic effect this can be ascribed, since such substitution would not change *g* values significantly. Such substitution does slow down CT quenching of the triplet ketone,[6] so perhaps a competing chemical reaction is responsible.

Net vs. Multiplet Effects. The dramatic change in the kind of CIDNP effect produced by para chlorination holds only for ^{19}F polarizations. Primarily multiplet ^1H and ^{13}C polarizations are observed for all ketones studied, although some net ^{13}C signals appear for the carbonyl carbon.

Table II. Predicted Net and Hyperfine Polarization Frequencies (MHz) for Different Nuclei of TFA

	$\Delta g(B/h)H_0$	M_jA_j (outer lines)
^{19}F	3.5	11.9
^{13}C	4.7	116
^{1}H	3.5	116

The stronger multiplet effects for the ^{1}H and ^{13}C nuclei relative to the ^{19}F of TFA can be explained in terms of the weak hyperfine splitting of ortho hydrogens in benzylic radicals. Equation 17 has been suggested by several authors[30b,64] to describe relative magnitudes of net and multiplet effects. We have left off terms not relevant to our radical pair.[65]

$$I_i \propto {}^1\!/_2 A_i[\Delta g(\beta/h)H_0 + \textstyle\sum A_jM_j] \qquad (17)$$

Relative net and multiplet intensities for each nucleus in TFA itself can be estimated from eq 17 with the following values of various parameters: $H_0(^{13}\text{C}) = 18.7$ kG; $H_0(^1\text{H}, ^{19}\text{F}) = 14.1$ kG; $(B/h) = 1.40 \times 10^6$ (G·s)$^{-1}$; $A_\text{F} = 27$ G $= 76$ MHz;[30] $A_{\text{H(ortho)}} \simeq -4.25$ G $= -11.9$ MHz;[66] g values in Scheme V. The predicted Zeeman and hyperfine frequencies are listed in Table II.

Use of an equation such as (17) represents only a partial analysis of polarization intensities and apparently overestimates the importance of multiplet effects relative to net effects, although the comparison depends strongly on the accuracy of the g-value estimates. However, as Table II indicates, the very weak hyperfine splitting by ortho hydrogens in radicals such as PhC(OH)CF$_3$ produces a relatively weak multiplet polarization of the ^{19}F resonance as split by those ortho protons. The corresponding multiplet polarizations of the ortho-H and ^{13}C resonances are relatively strong because they benefit from the large fluorine-hyperfine splitting in PhC(OH)CF$_3$. In reality, both ^{1}H and ^{19}F multiplet polarizations result from the same $A_\text{F}{\cdot}A_\text{H}$ term and must have comparable absolute intensities (subject to differing $T_{1\text{N}}$ values); the ^{19}F net effect is much more intense than the ^{1}H net effect because $A_\text{F} > A_\text{H}$.

Timing of Protonation. Our results in aromatic solvents certainly suggest that direct protonation of exciplexes is possible. Whether this also occurs in acetonitrile solvent depends on the lifetime of the exciplex. The acid-catalyzed CIDNP occurs over a wide range of DMB concentrations such that all the triplet mechanisms A seen in neutral solution at high [DMB] is offset by the strong acid-catalyzed E. Since our first report,[3] Roth has shown that for TFA/DMB low acid concentrations give an A/E ^{19}F multiplet while concentrations similar to those we employ give E.[2] He suggests that the A/E polarization expected from in-cage TFA$^-$·/DMB$^+$· decay is made observable by efficient protonation of escape TFA$^-$·. Degenerate H exchange between protonated ketyls and ground-state ketones is much slower than electron exchange between ketyl anion and ground-state ketones,[67] so that nuclear relaxation of escape ketyl becomes so efficient that the triplet mechanism loses intensity while escape polarization no longer coincidentally offsets in-cage radical pair polarization.

If low acid concentrations indeed turn off the triplet mechanism and maximize the polarization from in-cage decay of the TFA$^-$·/DMB$^+$· pair, then the change in polarization at higher acidities must be due to something besides simple protonation of free TFA$^-$·. Random encounters of PhC(OH)CF$_3$ and DMB$^+$· would produce the E observed, superimposed on a *strong* A/E multiplet. In fact there is a weak A/E component for TFA. However, with p-ClTFA the observed A/E multiplet would be superimposed on a strong A (from in-cage decay), of which there is no trace.

Protonation of either exciplex or initial radical ion pair would bypass polarization from a TFA$^-$·/DMB$^+$· pair and replace it with PhC(OH)CF$_3$/DMB$^+$· polarization. Since the exciplex is formed first and is known to be susceptible to protonation, the majority of PhC(OH)CF$_3$ formation at high acidities probably comes from protonation of the exciplex, provided that the exciplex lifetime is at least 10^{-9} s (to allow diffusion-controlled reaction with 0.1 M acid). Protonation of caged radical ion pairs is a possible competitive or alternative process.

The effect of CCl$_4$ on TFA/DMB CIDNP depicted in Figure 2 strongly resembles the effect of low acid concentration as reported by Roth.[2] Rapid oxidation of escape ketyl radicals by CCl$_4$ is possible but would have the same effect on both triplet and radical pair CIDNP mechanisms as high ketone concentration. We suspect that some ketyl-CCl$_4$ redox process produces small concentrations of HCl.

Acknowledgment. The nuclear polarizations produced by irradiation of TFA with electron donors have helped define more precisely two important problems: the equilibrium between protonated and unprotonated ketyl radicals and the limited importance of CIDNP derived from spin-polarized triplets. As regards the latter, we wish to thank Dr. Cynthia Chiu for performing the biphenyl quenching experiments, Professors Frank Adrian, Gerhard Closs, and Jeffrey Wan for helpful advice, Professor Adrian for a preprint of ref 29, and Dr. Heinz Roth for a most satisfying cooperative effort in interpreting our independent results. We thank the National Science Foundation for support of this work and the Institute of General Medical Sciences of the NIH for a postdoctoral fellowship (No. GM57549-01) to M.J.T.

References and Notes

(1) Thomas, M. J.; Wagner, P. J.; Manion-Schilling, M. L.; Roth, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 3842.

(2) Manion-Schilling, M. L.; Hutton, R. S.; Roth, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 7792.

(3) Thomas, M. J.; Wagner, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 3845.

(4) Wagner, P. J.; Leavitt, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 3669.

(5) Wagner, P. J.; Puchalski, A. E. *J. Am. Chem. Soc.* **1978**, *100*, 5948.

(6) Wagner, P. J.; Lam, H. M. H. *J. Am. Chem. Soc.*, preceding paper in this issue.

(7) (a) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769. (b) Wagner, P. J.; Kochevar, I. E. *Ibid.* **1968**, *90*, 2232. (c) Clark, W. D. K.; Litt, A. D.; Steel, C. *Ibid.* **1969**, *91*, 5413. (d) Porter, G.; Topp, M. R. *Proc. R. Soc. London, Ser. A.* **1970**, *315*, 163.

(8) Arimitsu, S.; Masuhara, H.; Mataga, N.; Subomura, H. *J. Phys. Chem.* **1975**, *79*, 1255.

(9) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834. *Isr. J. Chem.* **1970**, *8*, 259.

(10) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 839.

(11) Roth, H. D.; Lamola, A. A. *J. Am. Chem. Soc.* **1974**, *96*, 6270.

(12) McKinney, T. M.; Geske, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 3013.

(13) Zweig, A.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1964**, *86*, 4124.

(14) O'Donnell, J. F.; Ayres, J. T.; Mann, C. K. *Anal. Chem.* **1965**, *37*, 1161.

(15) Tomkiewicz, M.; Klein, M. P. *Rev. Sci. Instrum.* **1972**, *43*, 1206.

(16) Closs, G. L.; Paulson, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 7229.

(17) Kaptein, R. *Chem. Commun.* **1971**, 732.

(18) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(19) Rogers, M. J.; Whiffen, D. H. *J. Chem. Phys.* **1964**, *40*, 2662.

(20) For the benzyl radical, see: Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 4201.

(21) Willson, R. L.; Slater, T. F. In "Fast Processes in Radiation Chemistry and Biology," Adam, G. E., Fielder, E. M., Michael, B. D., Eds.; Wiley: New York, 1975; p 153.

(22) We assume a normal β-proton hyperfine splitting.

(23) (a) Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969; p 228. (b) Abraham, R. J.; Kemp, R. H. *J. Chem. Soc. B* **1971**, 1240.

(24) Wagner, P. J. In "Creation and Detection of the Excited State", Lamola, A. A., Ed.; Marcel Dekker: New York, 1971; Vol. IA, p 173.

(25) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 2820.

(26) Hammond, G. S.; Caldwell, R. A.; King, J. M.; Kristinsson, H.; Whitten, D. G. *Photochem. Photobiol.* **1968**, *7*, 695.

(27) This adjective, found in any English dictionary, was suggested to describe the common light-wasting process whereby some intermediate formed from an excited state reverts to ground-state reactant;[28] such situations have more recently been dubbed "cyclic photoreactions".[29]

(28) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1969**, *91*, 3085.

(29) Adrian, F. J.; Vvas, H. M.; Wan, J. K. S. *J. Chem. Phys.* **1976**, *65*, 1454.

(30) (a) Closs, G. L. *Adv. Magn. Reson.* **1976**, *8*, 1. (b) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251, 6262.
(31) Puchalski, A. E., unpublished work.
(32) Marshall, J. H., quoted in ref 2.
(33) Forbes, W. F.; Sullivan, P. D.; Wang, H. M. *J. Am. Chem. Soc.* **1967**, *89*, 2706. Sullivan, P. D. *J. Phys. Chem.* **1970**, *74*, 2563.
(34) (a) Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2537. (b) Hirota, N. In "Radical Ions", Kaiser, E. T., Kevan, L., Eds.; Interscience: New York, 1968; pp 75–83.
(35) Closs, G. L.; Doubleday, C. E.; Paulson, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 2185.
(36) Atkins, P. W.; Dobbs, A. J.; McLaughlan, K. A. *Chem. Phys. Lett.* **1974**, *29*, 616.
(37) (a) Atkins, P. W.; Buchanan, I. C.; Gurd, R. C.; McLaughlan, K. A.; Simpson, A. F. *Chem. Commun.* **1970**, 513. (b) Wong, S. K., Wan, J. K. S. *J. Chem. Phys.* **1973**, *59*, 3859.
(38) (a) Wong, S. K.; Wan, J. K. S. *J. Am. Chem. Soc.* **1972**, *94*, 7197. (b) Wong, S. K.; Hutchinson, D. A.; Wan, J. K. S. *J. Chem. Phys.* **1973**, *58*, 985. (c) Atkins, P. W.; Evans, G. T. *Chem. Phys. Lett.* **1974**, *25*, 108. *Mol. Phys.* **1974**, *27*, 1633. (d) Adrian, F. J. *J. Chem. Phys.* **1974**, *61*, 4875.
(39) (a) Bargon, J.; Fischer, H. *Z. Naturforsch. A* **1967**, *22*, 1556. (b) Lawler, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 5519. (c) Cocivera M. *Ibid.* **1968**, *90*, 3261.
(40) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1969**, *91*, 4549, 4550.
(41) El-Sayed, M. A. *Acc. Chem. Res.* **1971**, *4*, 23.
(42) Carrington, A.; McLachlan, A. D. "Introduction to Magnetic Resonance"; Harper and Row: New York, 1967; pp 231–233, 197–198.
(43) Adrian, F. J. *Chem. Phys. Lett.* **1971**, *10*, 71.
(44) Souto, M. A.; Wagner, P. J.; El-Sayed, M. A. *Chem. Phys.* **1974**, *6*, 193, and references cited therein.
(45) Harrigan, E. T.; Hirota, N. *Mol. Phys.* **1976**, *31*, 663.
(46) However, Professor J. Wan has kindly informed us that he has observed strong CIDEP emission of the phenoxy radical upon irradiation of TFA and phenol.
(47) Bukhtivarov, V. V.; Bubnov, N. N. *Teor. Eksp. Khim.* **1968**, *4*, 413.
(48) (a) Closs, G. L.; Trifunac, A. D. *J. Am. Chem. Soc.* **1970**, *92*, 2186. (b) Walling, C.; Lepley, A. R. *Ibid.* **1972**, *94*, 2007.
(49) Bartlett, P. D.; McBride, J. M. *Pure Appl. Chem.* **1967**, *15*, 89.
(50) Lontz, R. J. *J. Chem. Phys.* **1966**, *45*, 1339.
(51) This situation also holds for other β-F hyperfines.[19]
(52) $\omega_Z = g\beta H/h$ at 14 000 G.
(53) $\tau_R = 3kT/4\pi\eta a^3$; $a = 5$ Å, $\eta = 0.003$ P. However, there is evidence that the Stokes–Einstein expression may overestimate τ_R: Hutton, R. S.; Roth, H. D.; Manion-Schilling, M. L. *J. Chem. Phys.*, in press.
(54) Bryce-Smith, D.; Cox, G. B.; Gilbert, A. *Chem. Commun.* **1971**, 914.
(55) (a) Davidson, R. S.; Steiner, P. R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1357. (b) Wagner, P. J.; Ersfeld, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 4515.
(56) For acetone: Eiben, K.; Fessenden, R. W. *J. Phys. Chem.* **1971**, *75*, 1186. For Ph_2CO: Yoshida, H.; Warashima, T. *Bull. Chem. Soc. Jpn.* 1971, *44*, 2950.
(57) Carter, M. K.; Vincow, G. *J. Chem. Phys.* **1969**, *47*, 292.
(58) Reference 36b, p 66.
(59) (a) Mataga, N.; Taniguchi, Y.; Nishina, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 764. (b) Prochorow, J.; Bernard, E. *J. Lumin.* **1974**, *8*, 471.
(60) Sinclair, J.; Kivelson, D. *J. Phys. Chem.* **1968**, *90*, 5074.
(61) Levy, G. C.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972; p 27.
(62) Reference 42, p 14.
(63) (a) Moniz, W. B.; Poranski, C. F., Jr.; Sojka, S. A. *J. Org. Chem.* **1975**, *40*, 2946. (b) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970; p 136.
(64) (a) Ward, H. R.; Lawler, R. G. *Acc. Chem. Res.* **1972**, *5*, 18. (b) Fischer, H. *Z. Naturforsch. A.* **1970**, *25*, 1957.
(65) Most such equations contain $\hbar$, which provides frequencies in units of radians/s instead of Hz.
(66) (a) Carrington, A.; Smith, I. C. P. *Mol. Phys.* **1965**, *9*, 137. (b) Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1968**, *90*, 7155.
(67) For acetophenone: $10^3\ M^{-1}\ s^{-1} < k_{exchange} < 10^4\ M^{-1}\ s^{-1}$. A. E. Puchalski, unpublished work. For benzaldehyde: $k_{exchange} \sim 10^5\ M^{-1}\ s^{-1}$. Reference 16.

Synthesis and Characterization of "Tailed Picket Fence" Porphyrins

James P. Collman,*[1a] John I. Brauman,[1a] Kenneth M. Doxsee,[1a] Thomas R. Halbert,[1a] Edward Bunnenberg,[1a] Robert E. Linder,[1a] Gerd N. LaMar,[1b] John Del Gaudio,[1b] George Lang,[1c] and K. Spartalian[1c]

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305, the Department of Chemistry, University of California, Davis, Davis, California 95616, and the Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802.

Received July 23, 1979

Abstract: The synthesis of "picket fence" porphyrin derivatives bearing covalently attached axial bases is described. These porphyrins have been well characterized, primarily as the iron(II) complexes, *meso*-tri(α,α,α-*o*-pivalamidophenyl)-β-*o*-5-(*N*-imidazolyl)valeramidophenylporphyrinatoiron(II) and *meso*-tri(α,α,α-*o*-pivalamidophenyl)-β-*o*-4-(*N*-imidazolyl)butyramidophenylporphyrinatoiron(II), by UV/visible, MCD, ^1H NMR, and Mössbauer spectroscopy, magnetic susceptibility, and elemental analysis. Preliminary results of carbon monoxide binding studies are reported.

Introduction

The development of simple compounds modeling the reactivity of the oxygen transport and storage proteins hemoglobin (Hb)[51] and myoglobin (Mb) is of continuing interest.[2-4] A series of models has appeared in the literature,[2-11] and the reactions of these, both in solution[2b,c,3-10] and in the solid state,[11] have been extensively investigated. Recent studies have been directed toward the elucidation of the mechanism of cooperativity in hemoglobin. According to the Hoard-Perutz theory,[12] Hb has two alternative quaternary structures: the liganded, "R" state, in which the O_2 (and CO) affinity is essentially that of the isolated subunits, and the deoxy, "T" state, in which the O_2 (and CO) affinity is greatly diminished. Cobalt-reconstituted hemoglobin (CoHb) also demonstrates cooperativity in O_2 binding,[13] and for this reason model complexes of both iron and cobalt have been examined.

Solution studies demonstrated the capability of the "picket fence" porphyrin,[14] **2** (Figure 1), in which the "pickets" prevent irreversible oxidation, to mimic the O_2 affinity of the low-affinity, "T" state of Hb,[10] as well as that of CoMb and both the "R" (high affinity) and "T" states of CoHb.[15] Direct solution measurements of the O_2 affinities of possible models for Mb and the "R" state of Hb, however, are not possible with the "picket fence" system, owing to the equilibria

$$\mathrm{PFe} + \mathrm{L} \overset{K_1}{\rightleftharpoons} \mathrm{PFeL}$$

$$\mathrm{PFeL} + \mathrm{L} \overset{K_2}{\rightleftharpoons} \mathrm{PFeL_2}$$

where P represents the porphyrin ligand and $K_2 > K_1$ for sterically unhindered axial nitrogen bases.[16] A solution measurement would thus yield not the desired equilibrium constant

0002-7863/80/1502-4182$01.00/0