

directly by nuclear recoil. To produce the iodine-123, it is not necessary for carrier iodine to be present to produce the species; only the small amount of xenon-123 needs to be added. Studies are currently being undertaken to investigate the charge and excitation of the labeling species.

It is also seen that this reactive iodine species will label compounds of biological interest under carrier-free conditions. With enriched tellurium-122 as the target material, it is anticipated that millicurie quantities of labeled compounds can be prepared,¹² using the generator-produced species as the iodinating agent.

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(12) Sodt (ref 3) estimates ¹²³I yields of $\approx 100 \mu\text{Ci}/\mu\text{A hr}$; therefore, with a 5- μA beam irradiating to saturation in xenon-123 it should be possible to prepare $\approx 2 \text{ mCi}$ of ¹²³I.

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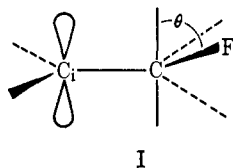
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The Angular Dependence of β -Fluorine Coupling Constants¹

Sir:

Several quite different proposals have been advanced concerning the origin and the angular dependence of the epr coupling constants of β -fluorine nuclei in free radicals. Strom and Bluhm² suggested that the coupling



constant would be greatest when θ is 90° (I) because the interaction³ between the p orbital centered on the carbon atom and the nonbonding p orbitals of the fluorine atom would be maximum in this conformation. In contrast, the results of an unrestricted SCF calculation in the INDO approximation indicate that the constant should be virtually zero when θ is 90° .⁴ Gerlock and Janzen⁵ suggest, on the other hand, that the minimum coupling might occur between 0 and 90° .

We have examined the rigid molecules II and III in which the β -fluorine nucleus is constrained to the nodal plane of the π electron system, $\theta = 90^\circ$, to assess the magnitude of the coupling constant for a fixed conformation.⁶ The spectroscopic observations are summarized under the structures.⁹ The assignments for II were

(1) This research was supported by the National Science Foundation under Grant No. GP-7448.

(2) E. T. Strom and A. L. Bluhm, *Chem. Commun.*, 115 (1966).

(3) W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965).

(4) K. Morokuma, *ibid.*, **91**, 2512 (1969).

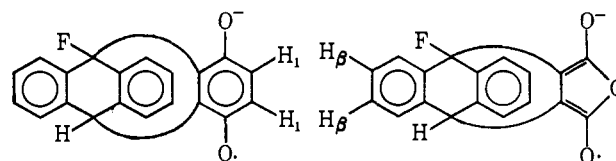
(5) J. L. Gerlock and E. G. Janzen, *J. Phys. Chem.*, **72**, 1832 (1968).

(6) The precursors to II and III were prepared by conventional methods^{7,8} and exhibited the expected analytical and spectroscopic properties.

(7) L. M. Stock and J. Suzuki, *J. Amer. Chem. Soc.*, **87**, 3909 (1965).

(8) S. F. Nelsen and E. D. Seppanen, *ibid.*, **89**, 5740 (1967).

verified by the examination of the deuterium derivative ($H_1 = D$).



II, $a_H = 2.6, 2.1 \text{ G}$ (2H), H_1
 $a_F = 0.85 \text{ G}$

III, $a_H = 0.13 \text{ G}$ (4H), H_β
 $a_F = 1.26 \text{ G}$

The results for the semiquinone and the semifurquinone both indicate that the ¹⁹F nucleus exhibits an important coupling when constrained to the nodal plane. For comparison, a_F for 2-trifluoromethylsemiquinone is only about 3-fold greater, 2.7 G. The a_F values for II and III are consistent with the greater electron density at C_2 of the semifurquinone; however, the difference between these constants is smaller than expected on the basis of hydrogen atom couplings.

Prior work prompted the conclusion that hyperconjugation between the p orbital on C_1 and the carbon-fluorine σ bond was not principally responsible for the coupling.⁷ The new results indicate, in addition, that a simple $\cos^2 \theta$ relationship is unsuitable for the description of the angular dependence. The finding that a_F is large for II and III together with the knowledge that the constants for such nuclei are highly anisotropic strongly infer that the nonbonding p electrons of the fluorine atom play an important role in the coupling mechanism.¹¹ Two quite different mechanisms are compatible with these data. On the one hand, an interaction between the p orbitals of fluorine and the π -electron density at C_2 would explain the results. The angular dependence predicted for such an interaction (based on the magnitude of the overlap integral¹² between the p orbital on C_1 and the nonbonding p orbitals of the fluorine atom) is shown in Figure 1. This relationship predicts that a_F for a trifluoromethyl group in free rotation should be about 2-fold greater than a_F for a fluorine atom constrained to the nodal plane. The available results, $a_{CF_3} = 2.77 \text{ G}$ and $a_F = 0.85 \text{ G}$, for the semiquinones suggest that the ratio is about 3. The discrepancy between these values is not excessive. Thus, the preliminary findings are consistent with the view that π -p interactions between the aromatic π system and the nonbonding p orbitals on the β -fluorine atom are important in magnetic resonance.¹³ On the other hand, the spin density observed for the fluorine nucleus in the nodal plane may result from a direct interaction between the oxygen and fluorine atoms of II and III.¹⁴ Further work will be necessary to assess the importance of this interaction at the internuclear

(9) The spectra were recorded as described previously.^{7,8,10} The proton assignments are based on previous results for other closely related compounds.^{7,10}

(10) K. E. Anderson, D. Kosman, C. J. Mayers, B. P. Rueckberg, and L. M. Stock, *J. Amer. Chem. Soc.*, **90**, 7168 (1968).

(11) (a) M. T. Rogers and D. H. Whiffen, *J. Chem. Phys.*, **40**, 2662 (1964); (b) R. J. Lontz, *ibid.*, **45**, 1339 (1966).

(12) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *ibid.*, **17**, 1248 (1949).

(13) Other experiments reveal that these interactions do not exert an important influence in reaction chemistry: F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, **89**, 5677 (1967).

(14) B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.*, **B**, 981 (1967).

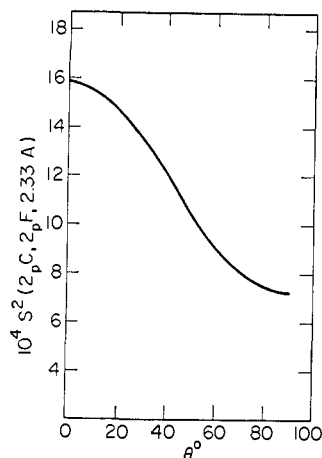


Figure 1. The relationship between S^2 for 2p orbitals centered on carbon and fluorine atoms separated by 2.33 Å and the dihedral angle θ shown in I. The S^2 value is sensitive to the selected structural parameters.

distance, over 2.5 Å, in the semiquinone and semifurquinone.

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Delayed Fluorescence and Phosphorescence of Aromatic Ketones in Solution

Sir:

The observation of emission from benzophenone^{1,2} and acetophenone² in fluorocarbon¹ and hydrocarbon² solvents represents a substantial breakthrough in the study of photochemical processes in solution. In the following we show that the emission from several aromatic ketones is composed of delayed fluorescence and phosphorescence components.

Sources of materials and purification methods will be described in the full paper. Solutions of the ketones in carbon tetrachloride or benzene were outgassed to $<10^{-5}$ mm using 5–7 freeze–pump–thaw cycles. Emission spectra were recorded using a Hitachi Model MPF-2A spectrophotometer (Phototube, Hitachi R-106). Corrected spectra and emission quantum yields were determined using quinine bisulfate as standard, $\phi_F = 0.56$.^{3–5}

The emission spectrum of benzophenone in carbon tetrachloride at 23° is typical (Figure 1). It agrees well with the spectra obtained in benzene, perfluoromethylcyclohexane,¹ and isooctane.² The positions of phosphorescence 0–0 bands and the corresponding triplet excitation energies are given in Table I. These energies are 1–2 kcal/mol lower than those obtained from measurements in hydrocarbon glass at 77°K.⁶ For the benzophenones a plot of E_T against Hammett's σ is

- (1) C. A. Parker, *Chem. Commun.*, 749 (1968).
- (2) W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).
- (3) J. E. Gill, *Photochem. Photobiol.*, **9**, 313 (1969).
- (4) J. W. Eastman, *ibid.*, **6**, 55 (1967).
- (5) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).
- (6) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

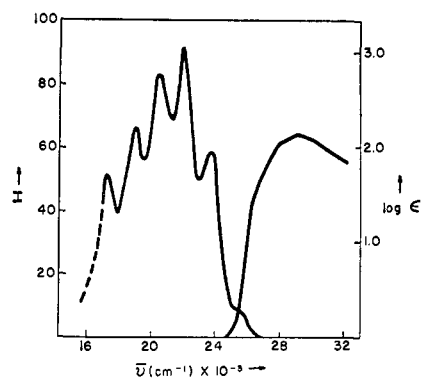


Figure 1. Corrected benzophenone emission spectrum in carbon tetrachloride: 23° on the left; $n-\pi^*$ absorption on the right.

fairly linear and gives $\rho = 1.03$, linear correlation coefficient $r = 0.916$.⁷ The positive value of ρ may reflect the increase in electron density at the carbonyl carbon upon $n-\pi^*$ excitation.⁸

Table I. Triplet Energies and Emission Bands of Aromatic Ketones in CCl_4 at 23°

Ketones X-PhCOPh-Y	E_T , kcal/mol	$S_0^0 \leftarrow T_0^1$, μm^{-1}	$S_0^0 \rightarrow S_0^1$, μm^{-1}
4,4'-diOMe	68.4	2.39	2.58
4-OMe	67.8	2.37	2.53
3,4'-diMe	67.5	2.36	2.54
H	67.6	2.36	2.52
3-CO ₂ Me	67.4	2.36	2.52
3-Cl	67.2	2.35	2.51
3,4'-diCl	66.8	2.34	2.49
4,5'-diCO ₂ Me	67.1	2.35	2.51
3,4'-diCO ₂ Me	66.0	2.31	2.46
X-PhCOMe			
H	72.0	2.52	2.65 ^a
4-Cl	71.5	2.50	2.62 ^a

^a The delayed fluorescence band was much weaker in the two acetophenones studied and these values should be regarded as very approximate.

Delayed Fluorescence. A general feature of the emission spectra is the presence of a low-intensity band on the high-energy side. In the case of benzophenone the excitation spectrum for emission at 2.52 μm^{-1} is identical with excitation spectra obtained by monitoring the emission at lower frequencies. The relative intensity of the high-energy band increases with temperature. A plot of the logarithm of the ratio of the emission intensity at 2.56 μm^{-1} to that at 2.06 μm^{-1} against T^{-1} is linear, $r = 0.995$, and gives $\Delta H = 4.4$ kcal/mol for the two emitting states. The $S_0^0-S_0^1$ $n-\pi^*$ absorption of benzophenone shows good overlap with the emission band at 2.52 μm^{-1} , Figure 1, and it can be seen that the enthalpy difference corresponds closely to the spectroscopic $S_0^1-T_0^1$ splitting. It follows, then, that the high-energy band is activation-controlled delayed

(7) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 172–192.

(8) The ρ value may be compared with $\rho = 0.54$ from a similar plot for E_T 's measured at 77°K,⁹ and $\rho = 0.58$ obtained for the rates of hydrogen abstraction by benzophenones.¹⁰ Change in reactivity has been attributed to variation in the extent of mixing between the low-lying $n-\pi^*$ and $\pi-\pi^*$ triplet states.¹⁰

(9) M. B. Burtleigh, Ph.D. Thesis, University of California, Riverside, 1966, p 72.

(10) N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).