fluorescence.[11,12] The entropy difference between the singlet and triplet n-π^* states can be estimated from eq 1, where I_F and I_P are the relative intensities of fluorescence and phosphorescence and k_F and k_P are the rates of radiative decay from the singlet and triplet state, respectively.

$$\log\frac{I_F}{I_P} = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.203R} - \log\frac{k_P}{k_F} \qquad (1)$$

Using $k_F = 1.4 \times 10^5$ sec^{-1} [13] and $k_P = 1.6 \times 10^2$ sec^{-1},[14] $\Delta S = -3.5$ eu is obtained which gives $\Delta F = 5.4$ kcal/mol at 23°. The calculated equilibrium constant at 23° is 1×10^{-4} and checks well with the observation that at this temperature fluorescence comprises ~10% of the total emission (Figure 1). The absence of prompt fluorescence in the spectra is demonstrated by the disappearance of the fluorescence band at low temperatures and the fact that in the presence of sufficient concentration of a triplet excitation acceptor to intercept more than 90% of benzophenone triplets, the relative intensity of fluorescence to phosphorescence remains unaltered. Approximated positions of delayed fluorescence bands for several aromatic ketones are given in Table I.

The presence of significant concentrations of S^1 molecules in equilibrium with T^1 molecules can be of great photochemical significance. T^1 states may serve as reservoirs of excited molecules whose photoreactions proceed from S^1 states. Effective reaction rates will then depend on the Boltzmann population of S^1 and should be strongly temperature dependent. For molecules with small S^1–T^1 energy gaps, quenching of a photoreaction by triplet excitation acceptors need not, as has been generally assumed, signify that the reactive state is the triplet of the donor. Clearly, the mechanisms of many photoreactions require reexamination.

The Lifetime of Benzophenone Triplets in Solution. Much of the chemistry of benzophenone triplets has been studied in benzene[15] or carbon tetrachloride[16] solutions. The lifetime of benzophenone triplets in these solvents is therefore of considerable interest, and, in the case of benzene, has been the subject of several investigations.[2,15] Stern–Volmer quenching constants of the emission at 23° were obtained with naphthalene as quencher in benzene and benzil as quencher in carbon tetrachloride (benzophenone, 5×10^{-3} *M*). Lifetimes of 8.4×10^{-6} and 1.1×10^{-4} sec for benzophenone triplets in benzene and carbon tetrachloride, respectively, were calculated using the value of k_q reported in ref 2.

The quantum yield of benzophenone phosphorescence in benzene at room temperature has been estimated at 2×10^{-4}.[17] An experimental value of 1.1×10^{-3} can be inferred from the results in ref 2.[18] Our measurements give emission quantum yields of 1.6×10^{-3} in benzene and 1.5×10^{-2} in carbon tetrachloride (benzophenone, ~5×10^{-3} *M*). The radiative lifetime of benzophenone triplets at 77°K in alcohol–ether glass is 6.4×10^{-3} sec.[14] Since ~10% of the emission at 23° is delayed fluorescence, the effective radiative lifetime should be ~5.7×10^{-3} sec. Using the actual lifetimes obtained from this work, the expected quantum yields are 1.5×10^{-3} and 1.9×10^{-2} for benzene and carbon tetrachloride, respectively,[19] in excellent agreement with our observations.

Reversible hydrogen abstraction from the solvent has been suggested as the path for rapid decay of benzophenone triplets in benzene.[1,20] Although benzophenone is photoreduced in pure benzene, the hydrogen abstraction rate is too slow to contribute significantly to the decay rate.[21] We propose that a major decay process may involve formation of an adduct diradical as has been suggested for the interaction of acetophenone triplets with alkenes.[22,23] The lifetime of benzophenone triplets in carbon tetrachloride is smaller than that in perfluorocarbon solvent.[1] The contributions of impurity quenching and/or external heavy atom effect in determining the decay rate in carbon tetrachloride remain to be assessed.

Acknowledgment. This research was supported by the National Science Foundation, Grant No. GP-7941, and by the Petroleum Research Fund, administered by the American Chemical Society. J. W. M. was also supported by the National Science Foundation, Grant No. GP-8015.

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Received September 25, 1969

High Resolution Nuclear Magnetic Resonance of Solid Perfluorohexane

Sir:

Temperature dependence in the structure of high resolution nmr spectra provides a well-known source of information about thermally activated molecular rate processes in solution.[1] Similarly, the temperature dependence of wide-line nmr spectra provides useful, if less detailed, information about the motions of molecules in crystals and polymers. We wish to point out that a new class of multiple-pulse nmr experiments[2] is capable of being employed in a similar spirit, with re-

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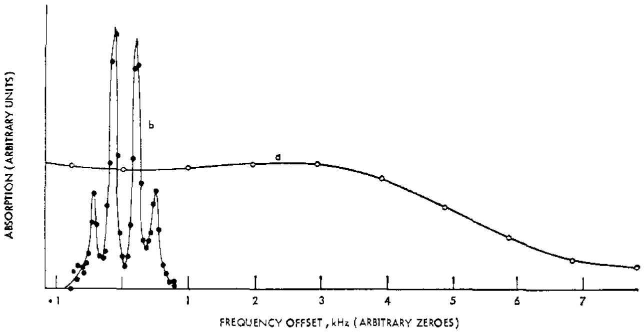

Figure 1. ^{19}F nmr spectra of solid C_6F_{12} at 200°K: (a) normal spectrum, from Fourier transformation of Bloch decay, showing restricted molecular rotation *in situ;* (b) multiple-pulse spectrum under the same conditions, showing lack of ring inversion.

sults that could not always be obtained by high resolution or wide-line methods, separately or together.

As an example, we consider perfluorocyclohexane. From a previous high resolution study[3] it is known that the spectrum of C_6F_{12} in solution at low temperatures consists approximately of an AB quartet, reflecting the presence of distinguishable interacting axial and equatorial fluorines (δ 18.2 ppm, $J = 284$ Hz). As the temperature is raised, a characteristic collapse to a single line occurs, indicating a rapid interconversion of conformers.

In Figure 1a we show the wide-line ^{19}F spectrum of solid C_6F_{12}, obtained at ~200°K by Fourier transformation of the Bloch decay, using a pulse spectrometer operating at 54.0 MHz. A barely resolved Pake doublet[4] is seen. While a detailed analysis of such a spectrum is difficult, the splitting appears to be consistent with a dominant dipolar interaction between geminal ^{19}F nuclei in a molecule which is rapidly rotating or reorienting about its "sixfold" axis. (Just below this temperature the spectrum rapidly broadens to a width consistent with a rigid lattice.)

We guessed that the mechanism of such a reorientation might involve a jump through 60°, accompanied by a chair–chair conformational flip to restore the molecule to harmonious packing with its neighbors. This is apparently *not* the case: the molecule rotates (through 120?) as a rigid entity. That this is so is evident from Figure 1b, which shows the spectrum obtained by Fourier transformation of the envelope of a multiple-pulse decay (WAHUHA spectrum) in solid C_6F_{12} at the same temperature. (This experiment employed a four-pulse cycle described elsewhere,[5] with a cycle time of 21 μsec and a 90° pulse width of 1.1 μsec.) Suppression of the dipolar broadening reveals the same AB quartet observed by Tiers[3] (δ 17.5 ± 1.5 ppm, $J = 310 \pm 40$ Hz). This shows that the molecule, as it rotates more rapidly than 6×10^4 sec^{-1}, is undergoing axial–equatorial interchange *less* rapidly than 1×10^3 sec^{-1}.

At higher temperatures the AB structure collapses: at 0° one sees a single line of ~300 Hz width. This is greater than our experimental resolution, indicating that AB collapse is not yet complete: the barrier to axial–equatorial interconversion may be very slightly greater in the solid than in solution.

No convincing evidence of a ^{19}F chemical shift anisotropy appears in any of our spectra, a situation which we find puzzling.

Acknowledgment. This work was supported in part by the National Science Foundation.

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Received October 20, 1969

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Oxidation by Metal Salts. VI. A New Chemical Method for the Generation of Aromatic Radical Cations

Sir:

Aromatic radical cations have been prepared by various techniques, but these have generally been limited to polynuclear aromatics having very low oxidation potentials.[1,2] Attempts to prepare the less stable radical cations of simple alkyl-substituted benzenes in solution by chemical oxidations have been relatively unsuccessful. It is the structure of these radical cations as determined by electron spin resonance spectroscopy that is most crucial in testing the various theoretical treatments of aromatic radical ions.

We now wish to report a new chemical oxidation method which, combined with a rapid mixing flow technique, permits the detection and characterization of aromatic radical cations. The chemical reaction involves the oxidation of the aromatic hydrocarbon by cobaltic ion, a process postulated to involve radical cation intermediates.[3] Pure trifluoroacetic acid was used as the solvent and ligand in order to increase the oxidation rate and stabilize the radical cation intermediate. In a typical procedure, 10^{-3} *M* solutions of the hydrocarbon in trifluoroacetic acid and cobaltic acetate in trifluoroacetic acid were rapidly mixed in a flow cell at room temperature. The total flow rate was usually in the range of 15–50 ml/min. By this technique, the esr spectra of hexamethylbenzene, pentamethylbenzene, and the various tetramethylbenzene radical cations were obtained. Radical cations derived from less alkylated aromatics such as 1,3,5-tri-*t*-butylbenzene and *p*-di-*t*-butylbenzene were also observed successfully.

The esr spectrum of the hexamethylbenzene radical cation in trifluoroacetic acid was similar to that reported for the radical cation prepared in sulfuric acid.[4,5] The spectrum consisted of at least 13 evenly spaced lines, with a hyperfine splitting constant of 6.45 G.[6] One carbon-13 splitting of 2.2 G was also observed. The average line width (measured between points of maxi-

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