Table VII. Calculated Force Constants for *tert*-Butyl Chloride Solution Model

Symmetry factored force constants, mdyn/Å[a]			
F_{11}	4.35	F_{12}	−0.244
F_{22}	2.740	F_{13}	0.851
F_{33}	0.965	F_{23}	−0.827
F_{44}	4.271	F_{45}	0.918
F_{55}	1.384	F_{46}	1.382
F_{66}	1.177	F_{56}	0.686

[a] All force constants associated with S_r assumed zero.

of 3.9–4.0 cm^{-1} for the low frequency (P_H) vibration of normal chlorides, the P_C band shift is less than the P_H band shift in cases of conformational splitting, even though the P_C band occurs at a higher frequency. Moreover, it is not clear whether the P_C shift is strongly or weakly dependent on alkyl chain size beyond *n*-butyl; there does still seem to be an appreciable effect between *n*-propyl and *n*-butyl. Thus, for kinetic isotope effect calculations involving longer chains, the P_H shift may be assumed to be near 4.0 cm^{-1} but further data may be necessary to establish a trend for the P_C shift. These isotopic labeling studies have thus led to a more complete correspondence between the relevant infrared vibrations and their molecular motions.

The model proposed adequately describes ground-state *tert*-butyl chloride molecules in gas phase and in methanol solutions, where only isotopic substitution on the chlorine is allowed. Diagonal force constants are reasonable when compared with literature values.[14,16,23] F_{22} is somewhat low, but this can be explained by the somewhat greater carbon–chlorine bond length.[22] Some off-diagonal constants are unusually large, but are justified by the strong mixing of modes, as shown both by the eigenvector calculations and the observed isotopic splittings of other modes. (The method of elimination of the redundant coordinate is also a factor and makes comparison of off-diagonal elements qualitative at best.) Perhaps the most interesting conclusion is that there is *no* vibration which is *principally* C–Cl stretch and that the vibration which has the largest carbon–chlorine contribution does not show the largest isotopic shift. Although this may be an artifact of the C_{3v} symmetry involved here, it does serve to emphasize that the common practice of labeling absorption bands with normal mode descriptions is at best approximate, and may be erroneous in some cases. Specifically, the common assumption that the nominal carbon–chlorine stretching frequency and isotopic shift alone are sufficient for simplified KIE calculations must fail for *tert*-butyl chloride, and may not be valid for other chlorocarbons. The model presented here successfully predicted all major frequency shifts and should, therefore, be directly applicable to the calculation of chlorine kinetic isotope effects in solution. In later papers[5,28] we shall discuss the results of simplified KIE calculations involving several ground-state vibrations and compare them with detailed computer-model transition state calculations.

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(28) R. C. Williams and J. W. Taylor, to be submitted.

Dynamic Nuclear Polarization in Phosphonitrilic Fluorides

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Abstract: Dynamic nuclear polarization has been observed in solutions of a series of phosphonitrilic fluorides $(PNF_2)_{n=3-7}$ with three free radicals. Generally, much weaker scalar coupling between the free radicals and the ^{31}P nuclei is found in the fluorides than in the corresponding chlorides. The alternating series trend and strong scalar couplings found for ^{31}P enhancements with the chlorides is not evident in ^{19}F enhancements with the free radicals bis(diphenylene)phenylallyl and galvinoxyl; in contrast, diphenylpicrylhydrazyl shows a strong scalar coupling to the ^{19}F nuclei which decreases monotonically with increasing ring size. Viewed by DNP, fluorine appears essentially unconjugated with the ring π-orbital system and behaves as on aliphatic hydrocarbons. The DNP results are correlated with other details of receptor molecular orbitals and radical-receptor collision attitudes.

Various properties of phosphonitrilic ring compounds of the type $(PNX_2)_n$ have been studied[2–5] to determine the nature of the bonding orbitals. In these molecules, a basic σ molecular framework is supplemented by a dual π system comprised of combinations of phosphorus 3d orbitals with the nitrogen valence shell orbitals. Dynamic nuclear polarization (DNP) with a variety of free radicals as probes responds to the receptor molecule electronic structure *via* stereospecific hyperfine interactions and thereby illuminates the

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(1) (a) Electronics Command; (b) British Columbia; (c) Rutgers, Sloan Foundation Fellow.

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nature of these orbitals. A DNP study[6] of the phosphonitrilic chlorides $(PNCl_2)_{n=3-7}$ indicated the Cl could transmit appreciable spin density to P. The detailed order of ^{31}P polarization within the series resulted from differing amounts of electron delocalization within the rings. These studies are now extended to the phosphonitrilic fluorides $(PNF_2)_{n=3-7}$. The goal of the present work is to compare the abilities of F and Cl to transmit spin coupling into the ring, and thereby deduce the effective aromaticity of the ring orbitals and their apparent conjugation with the exocyclic substituents.

Theory

Dynamic nuclear polarization of a receptor nucleus on one molecule by an unpaired electron on a second molecule can arise from two different types of interaction: magnetic dipolar coupling of the two spins, and scalar or contact coupling. Dipolar interaction couples spins directly through space and is dependent essentially on physical aspects of the molecular encounter: collision radii and diffusional correlation times. Dipolar coupling is always present in free-radical solutions and does not vary widely in magnitude; purely dipolar coupling produces negative nuclear polarization. In contrast, the scalar coupling component is conveyed to a significant degree by intervening electrons on the receptor molecule, and is thus sensitive to orbital disposition, bond type, and other chemical factors. The magnitude of the scalar component varies over a wide range. Pure scalar coupling results in positive nuclear polarization. The observed sign and magnitude of a nuclear enhancement reflect the relative magnitudes of the scalar and dipolar component.

In a recent paper, Dwek, *et al.*,[7] derived an expression for the effective free-electron spin density at the receptor nucleus, which governs the peak amplitude of the intermolecular scalar interaction.

$$\rho_N = \langle \psi_R^{(0)}(n+1) | \delta_N(r_{n+1}) | \psi_R^{(0)}(n+1) \rangle + 2\sum^{\text{occ}} \sum^{\text{unocc}} \frac{1}{{}^3\Delta E_M{}^{i\rightarrow i'}} \left\{ \sum_{P,Q,S,T} C_{iQ} C_{i'P} C_{i'S} C_{iT} \times \langle \chi_Q | \delta_N(r) | \chi_P \rangle \left\langle \chi_S \psi_R^{(0)} \frac{e^2}{r} \psi_R^{(0)} \chi_T \right\rangle \right\}$$

The spin density at a nucleus N during a radical–molecule collision is ρ_N. The first term is the square of the value of the radical-electron wave function $\psi_R^{(0)}(n+1)$ evaluated at the nucleus N. $\delta_N(r_{n+1})$ is the Dirac δ function. This term represents the direct interaction of the nucleus with the free-electron wave function. The second term in the expression for ρ_N represents the unpaired electron spin density generated at the nucleus by the perturbation of the receptor molecule paired electrons effected by the free radical. The double summation is over the i occupied and i' unoccupied receptor molecular orbitals. ${}^3\Delta E_M{}^{i\rightarrow i'}$ is the energy difference between the ground state of the receptor molecule electron and the excited state. This term arises in the denominator of the first-order correction to the ground-state wave function when it is mixed with the excited states in the perturbation treatment. The C_{iQ} are the coefficients for generation of molecular orbitals by a linear combination of the atomic orbitals χ_Q. Thus the second term reduces to the product of (1) a term inversely proportional to the ease of exciting the receptor electron,[8] (2) a term reflecting the value of the receptor molecule wave function at the nucleus, and (3) the perturbation integral coupling the ground and excited states.

Unfortunately, the parameters on which the equation for ρ_N are based are almost never quantitatively known. Only for the simplest systems could the coupling feasibly be calculated. Nonetheless, the expression serves as a useful guide for qualitative comparison of DNP in different molecular species.

Dwek, *et al.*,[7] also indicated the effect of the free-radical electron or electrons on bonding molecular orbitals which have some degree of polarity. They found that the more polar the bond, the less scalar coupling there is likely to be.

In all cases, dynamic nuclear polarization depends not only on the static magnitudes of the scalar and dipolar couplings, but also upon the frequency spectra of their modulation during the molecular encounter. At high magnetic field, molecular motions may be too slow to drive the transitions. At low field, this possibility is obviated. Fortunately, the amplitude and frequency spectrum of the scalar coupling are often sufficiently correlated to permit chemical interpretation using low-field data alone. This is true only for the scalar component, whose magnitude is strongly dependent upon the same collisional sticking tendencies which govern its frequency spectrum.

Experimental Section

Dynamic nuclear polarization measurements were taken at 24 ± 2° in a primary magnetic field of 75 G. At this field strength, the resonance frequencies of protons, ^{19}F nuclei, ^{31}P nuclei, and free-radical electrons are 319.7, 300.8, 129.4 kHz, and 210.7 MHz, respectively. The details of the experimental apparatus are given elsewhere.[9]

The intractable solubility of the quasialiphatic fluorides necessitated dilution of all samples in benzene and carbon tetrachloride in identical volume ratios $(PNF_2)_n:C_6H_6:CCl_4 = 1:2:3$. Samples were then made 0.02 *M* in the appropriate radical. Both ^{19}F and ^{31}P nmr signal strengths were seriously reduced such that some ^{19}F and all ^{31}P signals were below noise with optimum spectrometer settings, making signal accumulation necessary. Three factors which made low-field nmr detection difficult were (1) the low nuclear spin density resulting from the necessary dilution by inert solvent, (2) the intramolecular spin–spin coupling between ^{19}F and ^{31}P, and (3) the large nmr line widths of ^{31}P nuclei in these species. Because of these factors, unenhanced ^{31}P signals were beyond recovery within signal averager capacity (16,000 traces) and stability of the spectrometer. Thus, only the signs of the ^{31}P enhancements are reported, while both signs and magnitudes of the ^{19}F enhancements are given.

The phosphonitrilic fluorides were prepared as noted previously.[10] The radicals galvinoxyl (GALV) and diphenylpicrylhydrazyl (DPPH) were commercially available materials. Bis(diphenylene)phenylallyl (BDPA) was synthesized by Professor C. F. Koelsch. Solvents used were reagent grade commercial products. All samples were degassed and sealed in glass.

Results

Representative high-field nmr spectra for $(PNF_2)_6$ are shown in Figures 1 and 2. Hexafluorobenzene and

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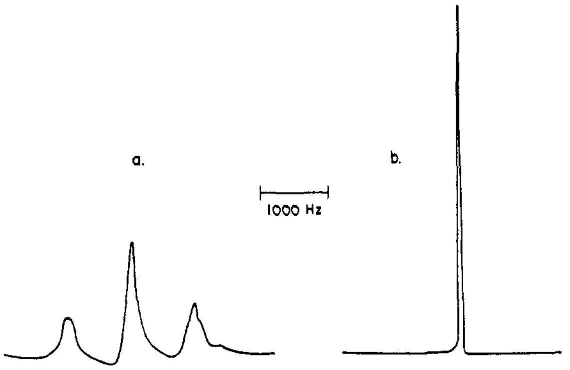

Figure 1. High-field nmr spectra of ^{31}P at 40.5 MHz: (a) neat $(PNF_2)_6$; (b) neat $(ETO)_3PO$. The $(PNF_2)_6$ resonance occurs 22 ppm downfield from H_3PO_4.

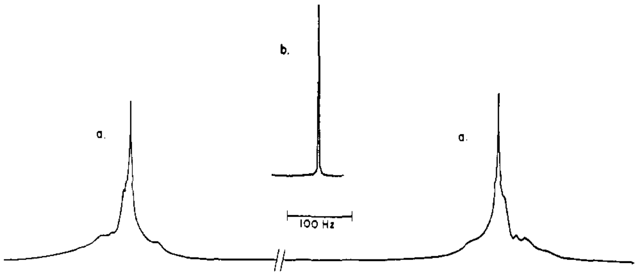

Figure 2. High-field nmr spectra of ^{19}F at 56.4 MHz: (a) neat $(PNF_2)_6$; (b) neat C_6F_6. The $(PNF_2)_6$ resonance occurs 97 ppm downfield from C_6F_6.

$(ETO)_3PO$ are included as comparison signals for ^{19}F and ^{31}P, respectively. The very much broader lines in $(PNF_2)_6$ are readily apparent. The line width of ^{31}P in $(PNF_2)_6$ is about 200 cps, which causes a substantial reduction of the signal-noise ratio in the low-field spectrometer. In the case of ^{19}F, the line width in $(PNF_2)_6$ is 8 cps, which in itself is not serious. Together with this, however, are the substantial fractions of the ^{19}F resonance in the line wings, and the 887 Hz ^{19}F–^{31}P spin–spin coupling. This splitting reduces the peak amplitudes of both the ^{19}F doublet and the ^{31}P triplet by 50% from normal singlet values.

Observed ^{19}F nmr enhancements are shown in Figure 3. Fluorine enhancements range from zero for the most positive samples (DPPH) to -250 for the most negative systems (GALV). The generally observed negative polarizations indicate that dipolar spin–spin coupling is dominant for the phosphonitrilic fluorides. With BDPA and GALV there is no significant variation in ^{19}F enhancement throughout the $(PNF_2)_n$ series, whereas with DPPH, enhancements become much more negative from the tetramer to the heptamer. Broadly, the scalar fraction of the fluorine nuclear polarization process increases in the order GALV < BDPA < DPPH. All ^{31}P nmr enhancements for $(PNF_2)_{n=3-7}$ with the three radicals are negative. This may be contrasted with DNP results[6] for $(PNCl_2)_{n=3-7}$ and the same radicals, which usually gave positive enhancements.

Discussion

The reduced proportion of scalar coupling for ^{31}P nuclei in the phosphonitrilic fluoride series, significantly less than in the chloride series, is consistent with

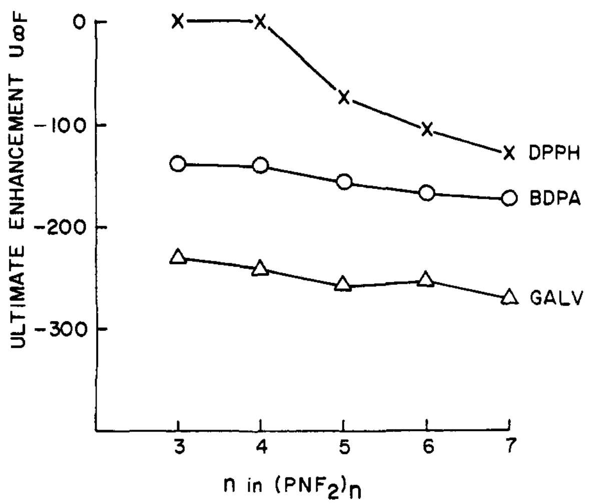

Figure 3. Dynamic nuclear polarization observed in solutions of free radicals and $(PNF_2)_{n=3-7}$.

the theory presented by Dwek, *et al.*[7] If radical collisions with the halogen atoms are primarily responsible for producing spin density at ^{31}P, one would expect more positive ^{31}P enhancements for the chlorides since the P–Cl bond is less polar than the P–F bond. Additionally, if collisions removed from the halogen (*e.g.*, collisions near N) provide the primary route for polarization, one would still expect F to allow for less scalar coupling than Cl since the ionization potentials of the chlorides are smaller than those of the corresponding fluorides.[5] Thus $^3\Delta E_M{}^{i\rightarrow i'}$ for Cl compounds should be generally lower than for the F analogs. Finally, the F atom is smaller than Cl, and the reduced collision radius strengthens the dipolar coupling. These low-field observations are consistent with previous DNP results[7] for ^{31}P obtained at high field (12,500 G), and have the advantage of reduced dependence upon the scalar frequency spectrum.

In the case of F, two collisional routes which polarize the nuclei must likewise be examined. A free radical may collide directly with the fluorine atoms and unpair electrons in orbitals localized on F. A second pathway originates with collisions at some other part of the molecule. The unpaired electron would interact with orbitals delocalized over N, P, and F to yield spin density at F. Delocalized receptor orbitals have the most favorable $^3\Delta E_M{}^{i\rightarrow i'}$, and thus provide the most reasonable means of long-range scalar interaction.

Direct collisions with F are expected to lead to large negative ^{19}F polarizations because the electrons about the F are quite tightly bound (ionization potentials *ca.* 16 eV).[5,8] Collisions involving delocalized π orbitals would in themselves favor positive enhancements because these electrons are less tightly bound (ionization potentials *ca.* 10 eV). The ionization potentials, however, of the homomorphic π orbitals show a conspicuous alternation[5] as ring size increases. If these orbitals are involved in the polarization process, one would expect alternating patterns in the ^{19}F DNP data. Likewise, contributions from the heteromorphic π system should be correlated with respective ionization potentials.

The facts clearly favor the direct polarization process. Fluorine enhancements with GALV rival the most negative ever found for F nuclei, equivalent to those of aliphatic fluorines. Further, the enhancement is constant with increase in ring size. The dominant mechanism must then be the direct radical–fluorine collision, with at most a minor contribution from the π systems.

BDPA behaves in a manner similar to GALV except that all ^{19}F enhancements with BDPA have larger scalar components. BDPA must also couple primarily with the ^{19}F directly, the larger scalar coupling resulting from a sterically more available unpaired electron on the radical.

The stronger scalar components in fluorine polarizations with DPPH cannot be readily explained solely on the basis of direct collision at the F site. Nevertheless, indirect scalar coupling *via* ring orbitals seems unlikely, since neither calculated nor observed ionization potentials for the two π systems can be correlated with the F polarizations.[5] A possible explanation for the DPPH results is longer lived collisions due to N–N attraction between radical and receptor molecules, but multifield DNP measurements would be required to assess this hypothesis.

In summary, DNP offers no evidence for spin coupling *via* either π system in $(PNF_2)_n$ with the three radicals tested. As a corollary, the ring π orbitals show no effects on the direct polarization of orbitals localized near fluorine. To a large extent, the exocyclic F atoms in $(PNF_2)_n$ behave toward radical probes as though they were not conjugated to the ring π orbitals. This situation is in marked contrast to that of F in fluorobenzenes or Cl in phosphonitrilic chlorides.

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Photochemistry of Benzaldehyde

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Abstract: The photochemistry of benzaldehyde has been studied by determining the quantum yields of benzene and carbon monoxide formation, benzaldehyde consumption and phosphorescence emission, and by following the phosphorescence lifetime over a range of pressure and excitation wavelengths. These data together with information from triplet transfer studies allow the construction of a model for the primary photochemical–photophysical processes (Figure 9) and the determination of most of the primary rate constants (Table II). Excitation with 276-nm light, $S_0 \rightarrow S_2$, results in the population of two vibrationally excited triplet states. At low pressures dissociation, yielding benzene and CO, occurs from the high vibrational levels of these states. Collisional deactivation of these states feeds the lower vibrational levels of the lowest triplet; from here there are no chemical decay channels and phosphorescence can be observed. In contrast to $S_0 \rightarrow S_2$ excitation, $S_0 \rightarrow S_1$ excitation results in no benzene or carbon monoxide formation and the phosphorescence yields are insensitive to pressure. There is however a significant quantum yield of benzaldehyde consumption and polymer formation can be observed.

As part of our work on the gas-phase photochemistry of azoalkanes[1] we have used benzaldehyde as a triplet energy donor.[2] Benzaldehyde is one of the few molecules which exhibits a strong phosphorescence in the gas phase,[3,4] and we believed that this emission would provide a very convenient monitor. Other workers have also used benzaldehyde as a triplet energy donor in the gas phase[5a] and in solution.[6,7] Our use of benzaldehyde as an energy donor was hampered by our lack of understanding of the photochemistry of benzaldehyde itself.

There were rather preliminary studies into the direct photolysis of gaseous benzaldehyde.[8–11] It has been reported that n → π^* excitation in the gas phase results in polymer formation and that at elevated temperatures the quantum yield of benzaldehyde consumption was as high as 40.[11] It has also been reported that at wavelengths below 270 nm benzaldehyde decomposed into benzene and carbon monoxide.[10]

The aim of this work was to obtain absolute quantum yields of the primary photophysical and photochemical processes and to study the effect of wavelength on the system. In this way we hoped to determine the mechanism for the population of the emitting state and determine from which state(s) dissociation into benzene and carbon monoxide occurred.

Experimental Section

Materials. All reagents were the best grade commercially available. The preparations of azoisopropane (AIP), 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH), and 2,3-diazabicyclo[2.2.2]oct-2-

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