If we assume the rate constant for O_2 quenching is roughly the same, we can imagine the following scheme.

$$R_2C{=}O^* \longrightarrow R_2C{=}O + h\nu \qquad k_P = 10^3$$

$$R_2CO^* + O_2\text{ (cage)} \longrightarrow R_2C{=}O + {}^1O_2 \qquad k_Q = 10^{11}$$

$$R_2C{=}O^* + O_2\text{ (adventitious)} \longrightarrow R_2C{=}O + {}^1O_2$$

$$k_Q' = k_{\text{diffusion}} \times [O_2] = 10^{11} \times 10^{-3} = 10^8$$

These rate constants indicate that only one excited carbonyl in 10^8 emits due to competition with quenching in the cage. Assuming a high efficiency of excited state production, the predicted maximum emission yield is 10^{-8}. The largest experimental yield is 4×10^{-8}. This means that excited carbonyl are indeed being produced with efficiencies of the order of unity. The adventitious O_2 quenching by 50% is probably due to a few excited carbonyls that escape from the cage before the dominant cage quenching occurs.

The ${}^1\Sigma$ O_2 can be produced by energy transfer or perhaps directly in the disproportionation reaction. Ogryzlo[18] has recently estimated the lifetime of the ${}^1\Sigma$ state in solution to be 10^{-9} sec. Since the radiative lifetime is 7 sec, the maximum observable photon yield is 1.4×10^{-10}. If we assume the observed count to be ${}^1\Sigma$ emission, the experimental yield is 0.9×10^{-11}, which is probably within experimental error of the maximum.

The apparent high selectivity of the disproportionation for the excited ketone triplet (rather than ground-state ketone and singlet O_2) should be predictable by a theoretical study of potential energy surfaces. The molecular framework involved in the concerted fragmentation is small enough so that this might be a feasible study.

Acknowledgment. The photon counting apparatus was designed and built by Mr. R. P. Schwenker. The cyclohexyl hydroperoxide was a gift from Dr. M. Rappaport. The author has also benefited from innumerable discussions with other workers in the field.

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Dynamic Nuclear Polarization in Phosphonitrilic Ring Compounds

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Abstract: A series of chlorinated phosphonitrilic ring compounds, ranging from $(PNCl_2)_3$ to $(PNCl_2)_7$, was examined by dynamic nuclear polarization with four different free radicals. A definite radical order was observed which suggests that enhancement details are related to the chemical properties of the ring compounds. The exocyclic chlorine atoms appear to be primarily responsible for the over-all magnitude of the intermolecular hyperfine coupling, while the detailed order of polarization within the series may be interpreted in terms of differing amounts of electron delocalization within the rings.

In recent years, numerous dynamic nuclear polarization (dnp) measurements have been reported for solutions containing free radicals in hydrocarbon[2] and fluorocarbon[3-5] solutions. For protons, only dipolar radical–solvent interactions are generally present, while for fluorine both dipolar and scalar hyperfine coupling are important. Furthermore, the chemical environment[6] of F considerably affects the degree of scalar coupling. This is conspicuously apparent when aromatic and aliphatic fluorocarbons are compared: aromatic fluorocarbons always show greater scalar coupling. In view of this, the degree of aromaticity in phosphonitrilic ring compounds, of concern for several years,[7-9] appeared to be an apt subject for study by dnp. Here, we report preliminary measurements for a graded sequence of phosphonitrilic ring compounds with only small differences between adjacent members. This approach should enable controlled isolation of factors related to the size and shape of the molecules. Because dnp is extremely sensitive to such variations, a better understanding of the nature of these compounds and their collisional interactions in solution should be obtained.

Theory

Dynamic enhancement of an nmr signal is effected by stimulating the resonance of a paramagnetic species

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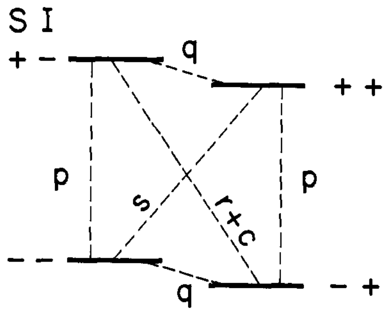

Figure 1. Energy levels and relaxation transitions for an electron and a nucleus of spin $^1/_2$.

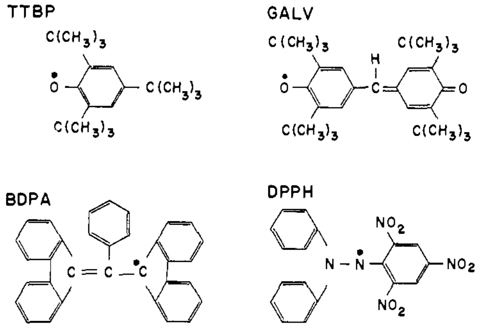

Figure 2. Structures of free radicals used to polarize phosphonitrilic compounds.

which is in a position to interact magnetically with a nucleus on a receptor molecule. In our case, both the magnetic nucleus and the odd electron have spin $^1/_2$, and the energy levels of the coupled spin system form a simple array (Figure 1). For this energy level scheme to apply, the nucleus and the electron, because they are on different compounds, must be coupled for a usefully long time period. The strength of the nmr signal is proportional to the steady-state population difference $(n_{++} + n_{-+}) - (n_{+-} + n_{--})$. At thermal equilibrium, these are determined by Boltzmann statistics if the energy of interaction between the spins is small compared to kT, which is true at the temperature of interest here.

Artificial stimulation of the epr transitions $(n_{++} \leftrightarrow n_{-+})$ and $(n_{+-} \leftrightarrow n_{--})$ tends to equalize populations such that $n_{++} = n_{-+}$ and $n_{+-} = n_{--}$. If molecular motions in the liquid occur at any of the frequencies corresponding to the energy differences between various levels, they may induce relaxation transitions p, q, r, s, c which tend to restore the original thermal equilibrium population distribution. The resultant population distribution is related to the relaxation rates in such a way that the nmr signal amplitude may be quite different from the equilibrium value. We have[10]

$$G = \frac{A}{A_0} - 1 = \left(\frac{\gamma_e}{\gamma_n}\right)\frac{r - s + c}{2q + r + s + c}\left(1 - \frac{T_1}{T_B}\right)S_e(P) \qquad (1)$$

The enhanced nmr amplitude is A, the equilibrium signal A_0; γ_e and γ_n are the gyromagnetic ratios of the electron and nucleus, respectively. The relaxation leakage factor $1 - (T_1/T_B)$ approaches unity for infinite radical concentration, as does the epr saturation function $S_e(P)$ for infinite saturation power. Thus, the ultimate enhancement U_∞ is[11]

$$U_\infty = (\gamma_e/\gamma_n)(r - s + c)(2q + r + s + c)^{-1} \qquad (2)$$

Relaxation transition probabilities $q, r,$ and s arise from magnetic dipole–dipole interactions; c arises from scalar hyperfine interactions. For purely dipolar coupling, $c = 0$, and for ^{31}P, the maximum nmr enhancement is -813 with $q/3 = r/2 = s/12$. For pure scalar interactions, $c \rightarrow \infty$ and $U_\infty \rightarrow +1625$. Corresponding values for ^{1}H are -329 and $+658$, respectively. Hence measurement of U_∞ for a given nucleus allows calculation of the total scalar relaxation rate relative to the total dipolar rate.

The chemical utility of dnp lies in the competition between dipolar and scalar coupling mechanisms. The strength of dipolar coupling depends on the electron–nucleus distance of closest approach d, and is a rather insensitive function of detailed molecular geometry. Scalar coupling also depends on d, but in a different way. It is proportional to the effective spin density of the unpaired electron at the nucleus and falls off with distance much more rapidly than the dipolar function.[12] Molecular geometry and stereochemistry thus play a crucial role. Moreover, and of even greater interest, scalar coupling may be transmitted to a nucleus not only by direct overlap of the wave functions, but also by the unpairing either of bonding electrons adjacent to the nucleus or of those in delocalized molecular orbitals.[13] Scalar coupling is thus very sensitive to many aspects of chemical bonding.

Experimental Details

Five phosphonitrilic ring compounds, $(PNCl_2)_n$, with n = 3–7 were chosen for study because preliminary dnp results with phosphorus compounds[14,15] indicated a striking polarization effect for Cl as a substituent. The compounds all have the same empirical formula which allows for a relatively straightforward interpretation, and further, many relevant physical and chemical parameters are known from other investigations.[7–9]

Four free radicals (Figure 2), each of differing geometry and electron distribution, were also chosen: bisdiphenylenephenylallyl (BDPA) and diphenylpicrylhydrazyl (DPPH), which contain moderately exposed spin density, and galvinoxyl (GALV) and tri-*t*-butylphenoxyl (TTBP), which, because of the *t*-butyl groups, are relatively well-shielded sterically. All samples were prepared 0.02 M in radicals, degassed by five freeze–pump–thaw cycles, and sealed in glass. To standardize viscosities and to provide a reference hydrogen nmr signal, 50% benzene was added to all samples. Of the resulting solutions, those with BDPA, DPPH, and TTBP were stable indefinitely, while those containing GALV lasted only a few hours.

Enhancements were measured at room temperature in a magnetic field at 74 G, for which the epr frequency is 210.7 MHz, the proton nmr frequency 319.7 kHz, and that for phosphorus 129.4 kHz. Unenhanced ^{31}P nmr signals were almost always within the noise and were measured by accumulation of 256 to 4096 traces on a signal averaging computer (CAT). In addition, up to 64 traces with the CAT were necessary to obtain satisfactory results for weakly enhanced signals (*e.g.*, $(PNCl_2)_5$ with DPPH).

For BDPA and TTBP, ultimate enhancements were obtained by direct extrapolation to infinite power. However, the epr line of DPPH was always too broad to be saturated completely, and for

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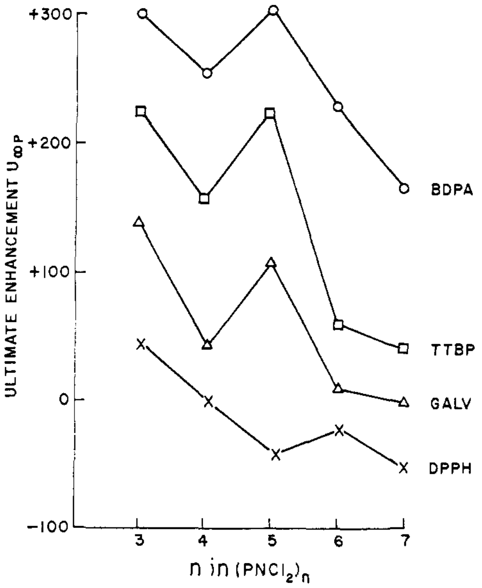

Figure 3. Extrapolated ^{31}P nmr enhancements for $(PNCl_2)_n$ compounds polarized with the four free radicals.

such samples, ^{31}P ultimate enhancements were computed by the ratio method.[6] This method was also used with several GALV samples to enable rapid comparisons before decomposition became critical.

Results

Ultimate ^{31}P enhancements for the various sample combinations are shown in Figure 3. U_∞ varies from -25 to $+300$, which corresponds to moderate scalar coupling, between 8 and 14 on the relative scale. These values are considerably lower than those observed for trivalent phosphorus with any radical. They lie between the values of -8 and $+500$ observed[15] for $C_6H_5P(O)Cl_2$ and $C_6H_5P(S)Cl_2$ which have a somewhat similar phosphorus environment.

The order of scalar coupling by radical type is consistently BDPA > TTBP > GALV > DPPH. This contrasts with the order observed[5,13] for fluorocarbons (BDPA > DPPH > TTBP > GALV) and with the somewhat more complex pattern observed[15] with noncyclic phosphorus compounds. Such a distinct radical order for the phosphonitrilics suggests a parallelism with the distinct order observed for the fluorobenzenes with the same radicals and the possibility of relating observed enhancements to specific properties of the receptor molecules.

As a function of increasing ring size, there is a general decrease in enhancement except that the pentamer is more positively enhanced than the tetramer with BDPA, TTBP, and GALV. The only other anomaly in the curves is the unexpected negative enhancement observed for DPPH with $(PNCl_2)_5$.

Discussion

General Comments on Intermolecular Spin Coupling. Two mechanisms[6] have been used to account for the transmission of scalar spin information: *exchange polarization*, analogous to the mechanism for intramolecular hyperfine coupling on free radicals, and *complex formation*. The former relates to the ability of the approaching odd electron to unpair solvent-bonding electrons, while in the latter case, the free electron interacts with low-lying empty solvent orbitals with consequent transfer of spin. Intramolecular exchange polarization, of course, can be an accessory to spin complex formation and the orbitals polarized can be either localized or delocalized. In reality, the mathematical description of the two processes has common elements,[13] and no definitive theoretical or experimental separation of the two will be attempted here.

Even though the detailed nature of the intermolecular coupling mechanism is open to debate, it has nonetheless been possible to postulate and observe several interesting general trends. Receptor electrons which are *a priori* expected to be polarizable turn out to be just that. For example, molecular orbital calculations and extensive experimental observations with fluorocarbons showed that fluorine near an aromatic system takes part in much stronger scalar coupling than aliphatic fluorines.[6] Radicals with sterically exposed odd electrons show stronger scalar coupling than well-shielded ones.[5] Poorly shielded phosphorus nuclei in trivalent phosphites show extremely strong scalar coupling in comparison with phosphates.[14,16]

For aromatic systems, it is tempting to postulate some degree of around-the-ring telemetry of spin polarization. Molecular orbital[13] calculations on fluorocarbons indicated that spin densities induced at fluorine nuclei far removed from the point of contact with the radical could on occasion exceed 25% of the primary density. Thus, although the augmented scalar coupling for aromatic fluorines arises largely from the sensitization of the local nuclear environment, contributions to and from distant nuclei cannot be ignored. Further, once the basic aromatic coupling mechanism is established, the effect of substituents may be larger than the direct aromatic contribution itself, perhaps because of changes in orbital energies with substitution.

Phosphonitrilic Systems. Since the observed enhancements depend primarily on the chemical properties of the $PNCl_2$ rings, we begin here by considering the bonding in such systems. After forming the required number of single bonds, some degree of electron delocalization is possible within the rings. This is usually considered in terms of interactions between the orbitals on P and combinations of the L-shell orbitals on N. In general, two types of π bonding are possible.[4] If the ring is planar a unique z direction perpendicular to the plane is defined. If the bisectors of the N–P–N, P–N–P angles are taken in local y axes, two phosphorus orbitals, d_{xz} and d_{yz}, contribute to π bonding perpendicular to the ring plane by overlap with $p\pi$ orbitals at nitrogen. A second (in-plane) π system can be formed by overlap of $d_{x^2-y^2}$, d_{xy}, and d_{z^2} with an sp_y hybrid at nitrogen; d_{z^2} contributes mainly to exocyclic π bonding and need not be considered further here. Either π system may be delocalized, *e.g.*, if one of the pair d_{xz}, d_{yz} or of the pair $d_{x^2-y^2}$, d_{xy} is appreciably more important than the other. Conversely, as the two components of a pair become more nearly equal, delocalization is restricted to three-center P–N–P regions, as has been suggested for the d_{xz}, d_{yz} pair.[17] The circumstances in which the "island" model can give a satisfactory account of the bonding have been determined.[8] For nonplanar rings, the situa-

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tion is similar, except that local coordinate systems originating at the various P atoms are used to describe the *z* direction for d-orbital quantization. For both types of rings, it should be reflected in the dnp results.

On the basis of dnp measurements of $C_6H_5P(O)Cl_2$ and $C_6H_5P(S)Cl_2$ with BDPA, the average magnitude of scalar coupling in the $PNCl_2$ compounds appears neither unusually high nor unusually low. Most noteworthy is the small range of enhancement. If Cl is replaced by NMe_2, there is only very weak scalar coupling transmitted to P (U_∞ for $P_3N_3(NMe_2)_6$ is highly negative). Thus, Cl appears to act either as a direct messenger of scalar spin information through coupling with the P-bonding electrons, or equally probably, as an effective activator of the bonding orbitals in the molecule, perhaps by reducing the energy gap between filled and empty electronic levels. The presence of exocyclic Cl atoms, then, accounts for the average magnitude of scalar coupling, and, if extensive delocalization is present, it is not as evident as for fluorocarbons. In fact, for the systems studied here, it must act as a small perturbation on the total scalar rate; hence it may be responsible for the order of polarization with ring size. We now enquire as to that possibility.

If the primary contribution causing the additional coupling came from island-type character or any other localized bonding scheme, we might expect *c* to depend in some manner on the local geometry near phosphorus and less on the over-all geometry of the ring. The average P–N–P ring angle increases from 120° for[18] $(PNCl_2)_3$ to 131° for[19,20] $(PNCl_2)_4$ to 148° for[21] $(PNCl_2)_5$, although the range of individual angles for the latter is large. Conversely, the N–P–N and Cl–P–Cl angles remain approximately the same with much smaller average deviations. Observed enhancements for the species indicate no such regular trend. On the other hand, only the trimer and pentamer are known to approximate planarity, and these compounds give the most positive enhancements with three of the four radicals. Now, while ring planarity as such need not be a criterion for long-range delocalization in phosphonitrilic compounds because of the angular dependence of the d orbitals, planarity would permit relatively well-shielded radicals to approach delocalized orbitals and unpair the electrons in them directly. But this type of collision, analogous to plane–plane collisions for aromatic fluorocarbons,[13] should not be of paramount importance here because the Cl atoms extend above and below the principal molecular surface. Planar collisions, moreover, are always expected to be weak for well-shielded TTBP and GALV. In this view, the detailed order of observed enhancements suggests the presence of delocalized orbitals in the PN rings.

The unexpected behavior of DPPH indicates a substantially different balance of intermolecular coupling routes. Over-all, the scalar coupling is much weaker than with BDPA, which, for fluorocarbons, it rivals by virtue of a similar degree of steric exposure of the unpaired electron. A further peculiarity is the lack of equality of coupling with $(PNCl_2)_3$ and $(PNCl_2)_5$. These observations suggest that spin transmission with DPPH proceeds primarily by a route which is differently influenced by aromaticity; *i.e.*, DPPH is apparently not able to couple effectively with the delocalized system. Moreover, the small scalar rates observed indicate some difficulty in coupling by any other route. This general weakness between DPPH and P has been noted for a more diverse selection of phosphorus compounds.[15]

A comparison of the structure and spin density distribution of the four radicals does not give an immediate clue regarding the proposed inability of DPPH to interact with a delocalized system. The answer must lie in stereospecific collision attitudes or in some as yet undefined principles of intermolecular spin transmission between radical and receptor atomic sites. It is not now possible to state which site or bond does respond to DPPH, but tests with substituents other than Cl should be illuminating. At present, we simply note that the failure of DPPH to mesh with a particular bonding system should accompany weaker over-all coupling, as is observed.

Last, we note that it seems possible to resolve the question of extensive delocalization further using dnp. This could be accomplished by comparing the polarization of hypothetical mono- or disubstituted compounds such as $P_5N_5(NMe_2)_9Cl$ with $P_5N_5(NMe_2)_{10}$. The latter should give large negative ^{31}P enhancements at low field, and Cl, which readily transmits spin information to P, should offer a window to any delocalized bonding system. Hence, the observation of positive enhancements for all P nuclei in the substituted compound would unequivocally demonstrate extensive delocalization.

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