example, the series of $H + X_2 \rightarrow HX + X$ (X = halogen) reactions serves as an example in which the vibrational energy of the newly formed HX molecule varies from 50 to 80% of the total energy released.[28] The cross sections for the reverse, endothermic reactions ($\Delta H_r^\circ =$ 30–50 kcal mol^{-1}) have been predicted to be highly peaked when most of the reactant energy is in the form of vibration.[42a] Even more dramatic are the results from molecular beam studies[43] as well as Monte Carlo calculations,[6,44–46] which show that for the reactions

$A + BC \rightarrow AB + C$ (A = Cs, K, Rb; BC = Br$_2$, I$_2$, ICl, IBr), more than 90% of the available energy is released in the vibrational mode of the product AB.

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Dynamic Polarization of Phosphorus Nuclei by Nitroxide Radicals

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Abstract: Dynamic nuclear polarization in six phosphorus compounds by four nitroxide radicals in liquid solution reveals several examples of stereospecific intermolecular hyperfine couplings. Trimethyl phosphate shows the expected weak scalar coupling with all four radicals. Di-*t*-butyl nitroxide and triacetone amine nitroxide fail to couple effectively with sterically unshielded phosphines and phosphites. These same two radicals show extremely strong coupling with dimethyl phosphite, suggesting a transient hydrogen bond $P-H\cdots O-N$.

$\mathbf{R}$ecent experiments[2] in dynamic nuclear polarization (dnp) have shown that free radicals can be used to probe the physical and chemical phenomena associated with molecular encounters in liquid solutions. Intermolecular hyperfine coupling in liquids depends on stereospecific interactions between certain atomic sites on radical and receptor molecules. The scalar coupling appears to reflect not only the static disposition of electronic orbitals on both molecules, but also the distortions of the orbitals as the two molecules come into contact. The investigation of molecular atomic sites and transient intermolecular bonding by dnp is conceptually complementary to the "spin-labeling" techniques,[3,4] which use either epr or nmr exclusively and depend on a more or less permanent attachment of molecules. Dnp is, of course, a combined epr–nmr technique, and functions diagnostically not only during firm attachment, but also during short-lived complexations and elastic collisions.

Phosphorus is especially well suited for dnp investigations; it has a nuclear spin $^1/_2$, a reasonably strong nmr signal, and is readily available in a great diversity of compounds. It is, moreover, an element of prime interest in the life sciences. Since nitroxides are highly

adaptable radicals for spin-labeling studies, we have examined dnp with an array of variegated phosphorus compounds in solution with nitroxides having different free-electron orbital disposition. The combinations were expected to show a variety of collisional interactions between the radical electron and the receptor P nuclei and to reveal varying propensities for complexation and transient bond formation.

Theory

The usefulness of dnp in study of molecular collisions arises from the scalar hyperfine interaction between the radical electron and the receptor nucleus. Intermolecular scalar coupling depends on the intimacy and duration of an encounter, the effective availability of the radical electron, and the responsiveness of the various spin-polarization pathways near the receptor nucleus. Strong spin coupling is found between atomic sites on radical and receptor molecules which share a tendency to form a bond. A strong interaction is also felt by receptor nuclei adjacent to such a site, or more distant, but connected to it by electron resonating structures. The latter can act as long-range carriers of spin information through their delocalized orbitals.

Both quantum mechanical and phenomenological theories for dnp have been presented in detail[5,6] and need no repetition here.

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Experimental Section

The radicals studied were di-*t*-butyl nitroxide (DTBN), diphenyl nitroxide (DPNO), dianisyl nitroxide (DANO), and 2,2,6,6-tetramethyl-4-piperidone-1-oxyl (TANO). The latter abbreviation stands for triacetone amine nitroxide, an accepted name which reflects the sequence of steps in its synthesis. The structures are shown in Figure 1.

Six phosphorus compounds were selected to examine the effects of different substituents and bonding orbital disposition: trimethyl phosphate, $(MeO)_3PO$; trimethyl phosphite, $(MeO)_3P$; dimethyl phosphite, $(MeO)_2PH(O)$; triphenylphosphine, $(Ph)_3P$; tri-*n*-butylphosphine, $(n-Bu)_3P$; and hexamethylphosphoramide, $(Me_2N)_3PO$.

The radicals were dissolved at a nominal concentration of 0.02 M in liquid solutions consisting of 50% (v/v) benzene and 50% of the desired phosphorus compound. Benzene was used to standardize samples, since a number of interesting phosphorus compounds (to be studied later) are solids at room temperature. Samples were deoxygenated and sealed in glass.

The dnp equipment and procedures were essentially identical with those described earlier.[7] The ratio method was used to compute P enhancements, because most nitroxide solutions have a multiplet epr line which cannot be feasibly saturated. Most samples were stable for at least several days, which allowed the long periods of signal accumulation needed for weak unenhanced nmr signals (up to 16,384 accumulations). All experiments were run in a field of 74 G at 23 ± 2°.

Results and Discussion

The experimental enhancement for all 24 radical–phosphorus combinations are presented in Table I,

Table I. Phosphorus Nmr Signal Enhancement, U_∞, by Dnp with Nitroxide Radicals

Receptor	DTBN	TANO	DPNO	DANO
$(MeO)_3PO$	−500	−420	−380	−580
$(Me_2N)_3PO$	−560	−300	−400	−280
$(MeO)_3P$	−85	+100	+840	+700
$(Ph)_3P$	−80	+100	+520	+530
$(n-Bu)_3P$	−230	+10	+850	+360
$(MeO)_2PH(O)$	+950	+940	+520	+150

and the computed scalar hyperfine relaxation component is given in Table II. A first inspection of the

Table II. Intermolecular Scalar Hyperfine Relaxation Component, c, in Solutions of Phosphorus Compounds and Free Radicals

Receptor	DTBN	TANO	DPNO	DANO
$(MeO)_3PO$	2.0	2.8	3.2	1.4
$(Me_2N)_3PO$	1.5	4.2	3.0	4.4
$(MeO)_3P$	6.8	9.6	35	27
$(Ph)_3P$	6.9	9.6	20	20
$(n-Bu)_3P$	4.9	8.1	36	15
$(MeO)_2PH(O)$	44	43	20	11

tables reveals that the four radicals fall into two classes, DTBN–TANO and DPNO–DANO, on the basis of nmr enhancements with the six phosphorus compounds. Such a grouping is reasonable in view of other properties of the radicals. In DPNO and DANO,[8] the free electron is partially delocalized into the aromatic rings. This allows additional opportunities for stereospecific collision with atomic sites of different hyperfine coupling propensity. In DTBN[9] and TANO,[10] however,

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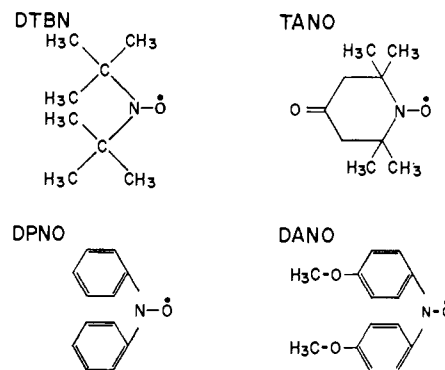

Figure 1. Nitroxide radicals used to polarize phosphorus nuclei.

the attached groups are unsuitable hosts for any peripheral spin delocalization; the free electron is highly concentrated in the NO region. A further visual difference is the much deeper color of DANO and DPNO, which is consistent with the wider distribution of the free electron. In view of these factors, it would be predicted that the two classes of radicals, DTBN–TANO and DANO–DPNO, will show different scalar hyperfine couplings in those situations where chemically sensitive stereospecific collisions are important.

The two well-shielded pentavalent receptors, $(MeO)_3PO$ and $(Me_2N)_3PO$, show the expected[2] weak scalar coupling with all four radicals. DPNO and DANO produce predictably[11] strong coupling with each of the three trivalent receptors, $(MeO)_3P$, $(Ph)_3P$, and $(n-Bu)_3P$. None of these cases warrants further discussion.

TANO and DTBN, nonetheless, show only moderate scalar couplings with the trivalent compounds. In the case of TANO, the oxygen *para* to the NO may be attracted preferentially toward phosphorus during collision, thus keeping the radical electron (concentrated on N) at a distance from the receptor nucleus. But this explanation is inapplicable to DTBN, since an analogous complexation tendency at the "back-side" of the molecule, upon or between inert *t*-butyl groups, seems unlikely. It is conceivable that trivalent phosphorus, in its role as electron donor,[12] is inhibited by a high formal negative charge due to the large electron density at the NO positions on DTBN[9] and TANO,[10] and the hyperfine coupling is thereby rendered very weak. Hyperfine coupling is equally well transmitted by either reception or donation of a single unpaired electron spin. The evidence indicates that the scalar coupling in these cases is transmitted by the "reverse" path of electron donation tendencies from receptor to radical.

Surprisingly large scalar coupling is observed with $(MeO)_2PH(O)$ and two of the nitroxides, DTBN and TANO. The pentavalent phosphorus in $(MeO)_2$-PH(O) is only moderately shielded, because of the small size of the hydrogen directly linked to phosphorus. Quite reasonably, $(MeO)_2PH(O)$ shows scalar coupling

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with most radicals which is intermediate between that of $(MeO)_3P$ and $(MeO)_3PO$. The large couplings with DTBN and TANO suggest asymmetrical hydrogen bonding, $P-H\cdots O-N$, between radical and receptor.[13] Such a view was earlier suggested from a much weaker scalar effect with tri-t-butylphenoxyl radical.[2] The strongest effects here are with TANO and DTBN, in which the free electron is highly localized to the NO group, rather than being delocalized into a π ring orbital. Not only is the available spin density high, but the molecule is probably more highly polar,[14] with negative charge on the NO group to favor H bonding. In this view, the moderate scalar coupling shown with DANO reflects an electron distribution which reduces

the hydrogen-bonding tendency, and also offers a smaller unpaired spin density at the active NO site.

The nmr signal of the bonding proton (presuming that transient H bonding does indeed exist here) is a 700-Hz doublet because of nuclear spin–spin coupling with P. It is observable at 74 G and shows essentially the full dipolar coupling with the radical electron. In consideration of the proton's centralized position in an H bond, it may seem surprising that it feels no scalar coupling, particularly since scalar coupling is transmitted over the proton from radical to phosphorus. The absence of scalar coupling at H is, however, consistent with either an electrostatic H bond or with a bond involving only π orbitals. These four samples would be of special interest in a multifield dnp study, where the effects of coupling strength and complexation time could be separately delineated.

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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. IV. Internal Rotation in Hydrocarbons Using a Minimal Slater-Type Basis

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Abstract: Self-consistent molecular orbital theory with a minimal basis of atomic orbitals is used to study internal rotation in hydrocarbons with two, three, or four carbon atoms. For the range of conformations in which steric interactions are not strong, calculated energy differences are found to be insensitive to the choice of bond lengths and bond angles. However, if steric interactions are large, the rigid rotor model is found to be inadequate. Good results are then obtained with a flexible rotor model in which each CCC angle is separately optimized for each conformation considered.

A number of workers have successfully used *ab initio* LCAO SCF MO calculations to calculate barriers to rotation of methyl groups[1-15] and to investigate the conformations of some important hydrocarbons.[15-17] In general, the results obtained are in good agreement with experiment. It has been found[18] that values of the rotational barriers are not particularly sensitive to the basis set employed.

In the work reported so far, only small numbers of molecules have been treated. It was of interest to apply

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a uniform model to a larger set of molecules, and in this paper we report the results of such a study on 19 hydrocarbons through C_4. We use a level of calculation (STO-3G) which has been described previously[19] and develop a procedure which may be generally applied to a large set of molecules. In addition, we examine the form of the potential function required to describe the rotation in the various molecules.

Potential Energy Functions

The potential energy function $V(\alpha)$ describing the internal rotation of one part of a molecule (rotor) relative to the remainder (framework) may be expanded as a Fourier series

$$V(\alpha) = \sum_i \frac{1}{2}V_{Ni}(1 - \cos iN\alpha) \tag{1}$$

where α is the angle of rotation and N represents the degree of symmetry of the molecule. In general, α is taken as zero for the minimum energy conformation. Thus, for example, for ethane, in which the rotating methyl group has threefold symmetry, $N = 3$ and the potential function may be written

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