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The magnetic resonance properties of the phosphorus-31 nucleus, the only naturally occurring isotope of the element, have been studied since the beginnings of NMR spectroscopy. While a very large number of compounds have been examined, and the technique has gained wide acceptance as a tool for exploring structure in both organic and inorganic phosphorus compounds, the theoretical aspects have not achieved the degree of development that provides ready explanations for many of the chemical shift effects and other properties that have been observed and

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20. ABSTRACT CONTINUED

continue to be observed. The research reported here was prompted by numerous first-hand encounters with the consequences of this lack of interpretive capability in the field, and several experimental projects were designed to provide information on particular structural-spectral effects. Theoretical work was simultaneously commenced so as to provide a basis for understanding the interactions involved, both of bonding and non-bonding origin. This dual attack has indeed led to some significant observations. Results are summarized in this Report in two sections. The first is concerned with the experimental work, while the second section is concerned with the theoretical work.

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EXPERIMENTAL AND THEORETICAL INVESTIGATIONS of ^{31}P NMR PHENOMENA

ARO Grant DAAG29-G-0267

Submitted to the U. S. Army Research Office

by

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For the Period: June 1, 1976 to May 31, 1979

L. D. Quin

D. B. Chesnut

I. INTRODUCTION

The magnetic resonance properties of the ^{31}P nucleus, the only naturally occurring isotope of the element, have been studied since the beginnings of NMR spectroscopy. While a very large number of compounds have been examined, and the technique has gained wide acceptance as a tool for exploring structure in both organic and inorganic phosphorus compounds, the theoretical aspects have not achieved the degree of development that provides ready explanations for many of the chemical shift effects and other properties that have been observed and continue to be observed. The research proposal to ARO was prompted by numerous first-hand encounters with the consequences of this lack of interpretive capability in the field, and several experimental projects were designed to provide information on particular structural-spectral effects. Simultaneously, it was proposed that theoretical work be commenced so as to provide a basis for understanding the interactions involved, both of bonding and non-bonding origin. This dual attack, coordinated by frequent contact between the two research groups involved (experimental, L. D. Quin; theoretical, D. B. Chesnut), has indeed led to some significant observations. Results are summarized in this Report in two sections. The first is concerned with the experimental work, while the second section is concerned with the theoretical work.

II. Experimental Program

1. Introduction

In initiating this research program, it was felt early consideration should be given to clarifying the effects of conformational influences on ^{31}P shifts. Within a family of non-cyclic phosphorus compounds, shifts are understandable on the same basis as ^{13}C shifts[1], and even if theory is deficient for both areas, at least empirical rules do exist that allow fairly easy interpretation of experimental results. However, anomalies abound among cyclic compounds; cases are known where only a difference in steric disposition of a phosphorus function, all other features being constant, produces a marked spread in ^{31}P values. Our work began with two systems of reasonably rigid carbon framework, so as to minimize the number of structural differences that could affect ^{31}P. We sought first to assess the result of coplanar δ-carbon interaction on ^{31}P shifts, for in ^{13}C NMR such carbons when in close steric proximity to a given nucleus can produce deshielding effects. For this study, we chose to use the naphthalene ring with a phosphorus substituent in the 1-position, and a methyl group at the 8-position acting as the crowding coplanar δ-carbon. As it developed, our synthetic work (discussed in part 2) led to certain compounds providing information on ring conformational effects as well. The work was expanded to include synthesis of some phenanthrenes with the same structural feature. Our second major objective was to prepare compounds with rigid ring systems but with two possible sites for a phosphorus substituent, differing only in the way non-bonded interactions could develop. For this study we chose the skeleton of the bicyclo[2.2.1]heptane system. Saturated (norbornane) derivatives were prepared with phosphorus at the 7-position and at both <u>exo</u>

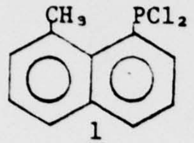
and endo sites of the 2-position. The unsaturated (norbornene) system was prepared with phosphorus at both syn and anti sites at the 7-position. The many compounds prepared have been of value not only in developing our understanding of ^{31}P shifts, but also in the area of ^{13}C NMR of phosphorus compounds, in particular with regard to the control of vicinal (3-bond) ^{13}C-^{31}P coupling. Our various results with the bicyclo[2.2.1]heptane derivatives are described in part 3.

As the work progressed in the above areas, results coming in from other studies in this Laboratory pointed to new directions to follow in our general concern with ^{31}P shifts. Thus, we developed a new synthetic approach to large-ring P compounds, stirring up interest in the importance of ring size (and hence bond and torsion angles) on ^{31}P shifts. We included on the present project some attempts at developing a better, more versatile method for preparing 3-membered rings, which system is characterized (at least with trivalent P) by remarkably high-field shifts. This work did provide some useful new information, especially with regard to the ^{31}P spectra and the nature of the complex formed between P(III) halides and aluminum halides. Contrary to literature indications, our results support a molecular, not an ionic structure. This work has now been published in full[2], and since it failed to provide compounds of use in our ring study, it will not be further discussed in this Progress Report. We have, however, acquired considerable ^{31}P data on rings of 7,8 and 9 members and this is discussed in Section 4. Another continuing study in our Laboratory on phospholes and derivatives led to some surprising observations on both ^{31}P shift effects and P-P coupling through three bonds, and pertinent results are given in Section 5.

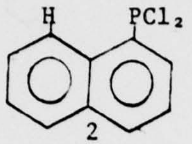
Our concern with the above problems has left untouched some areas of research presented in our original proposal. However, we feel that the emphasis we have given the more promising areas is justified, and that a good background has been laid for continuing our studies on ^{31}P NMR effects.

2. Phosphorus Substituents on the Naphthalene and Phenanthrene Systems

Attempts to prepare compound 1 for comparison of its ^{31}P shift with the des-methyl counterpart 2 were largely unsuccessful.



1



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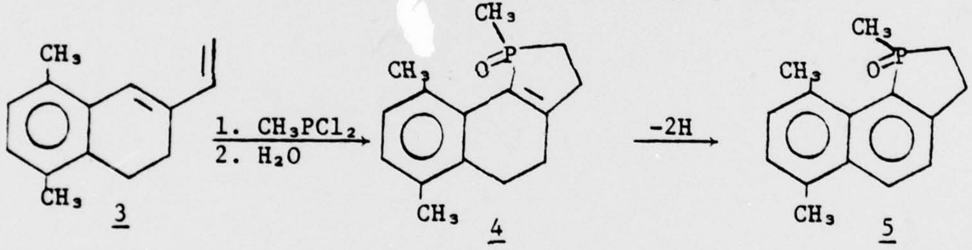
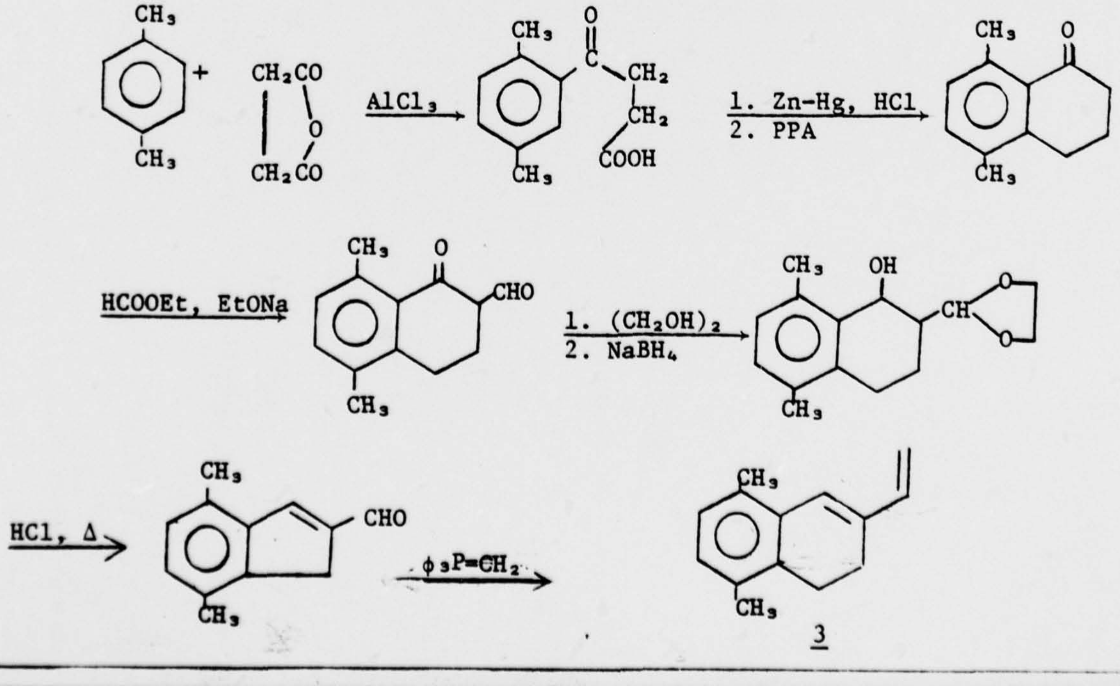
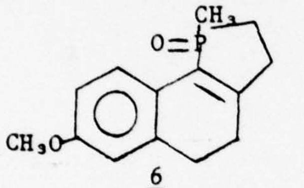
Syntheses depending on introduction of substituents in the 1,8 (peri) positions of naphthalene are known to be difficult, and we then diverted our efforts from such processes towards an indirect method for obtaining the same structure, albeit with the P atom in a ring system.



New diene 3 was successfully prepared from a tetralone by a route we have developed for the derivative without methyl groups.[3]



The McCormack reaction with diene 3 then provided phospholene oxide 4, which presented unusual purification problems now fully solved. Dehydrogenation to the naphthalene 5, a process we have applied successfully to several other related McCormack products^4 will soon be performed, thus arriving at the desired 1,8-substitution. We are doubtful, however, that any great ^{31}P effect is going to be seen, for we already know that the ^{31}P shift of dihydro compound 4 (+64.6; all ^{31}P shifts in this document are referenced to 85% H_3PO_4 , with + signs downfield,-upfield), which would only have small differences in geometry near phosphorus from the fully aromatic compound, differs very little from that of a des-methyl model (6, +63.6), prepared for other reasons in this Laboratory^{3b}.



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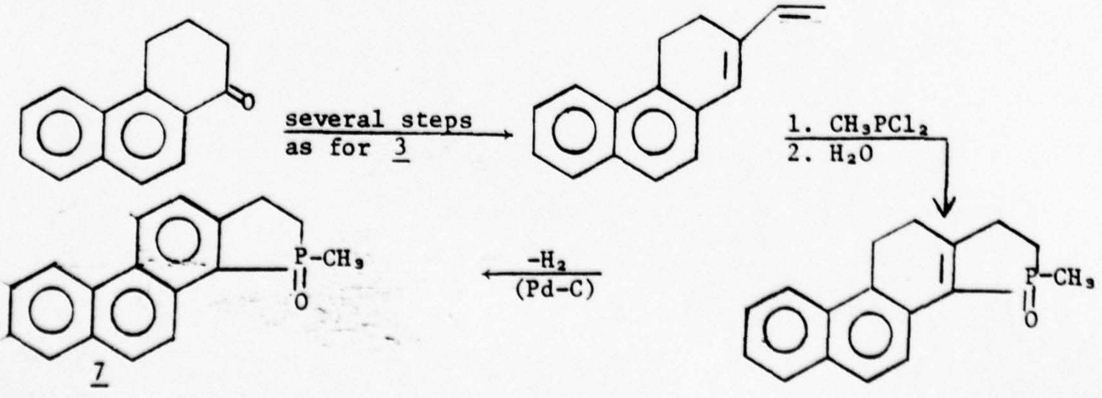
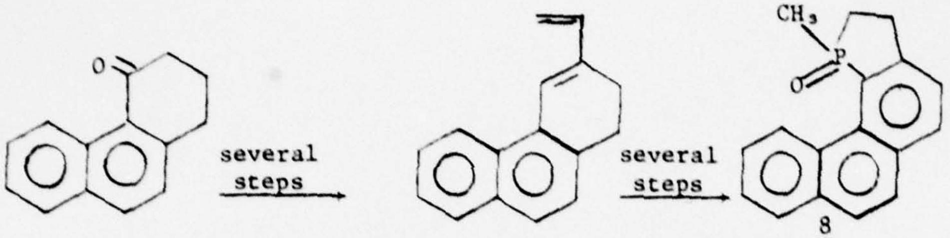
Since it is experimentally difficult to reproduce ^{31}P shifts on phosphine oxides to within 0.5-1.0 ppm due to their hydration tendencies, we do not believe the $\Delta\delta$ of 1.0 ppm observed here is significant. Phosphines in this series will also be prepared since their ^{31}P shifts cover a much broader range and are thus more sensitive to structural effects.

In another approach to establishing model compounds with crowding coplanar δ-substituents, we are seeking phenanthrene derivatives 7 and 8. In the latter, a carbon of a benzene ring can be considered to produce the desired δ-crowding. Compound 7 has already been prepared, and found to have a ^{31}P shift of +60.0:



Compound 8 will be prepared similarly from an isomeric ketone:



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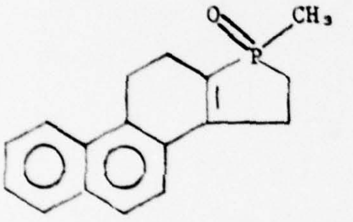
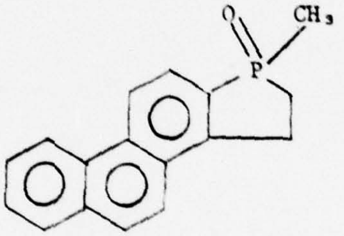
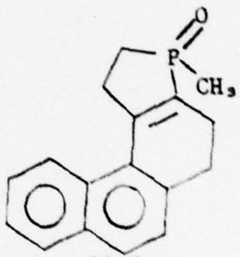
The intermediate diene has already been synthesized. Other new phenanthrene derivatives also prepared and characterized in this phase of our study to aid in assessing δ-effects are:



9, $\delta^{31}P = +65.5$

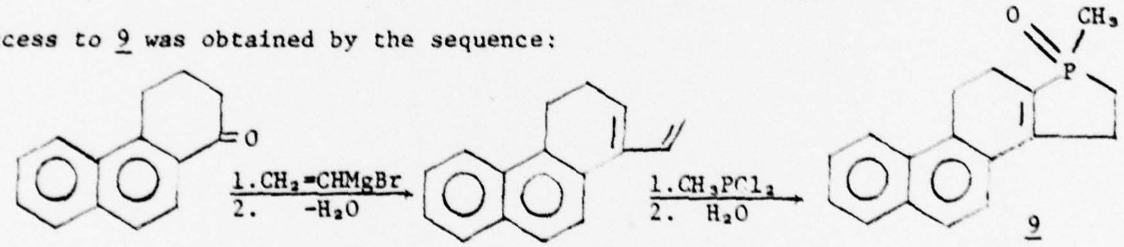


10, +60.4



11, +72.8

Access to 9 was obtained by the sequence:



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Compound 11 was similarly obtained from the isomeric ketone. The difference in ^{31}P shifts for 9 and 10 is notable; an important steric effect is involved, as will be discussed in the next section.

While much progress has been made, considerable work remains to be done to complete the syntheses of the model sterically crowded structures. The novelty of these structures makes them quite valuable targets, however, and the entire project represents the first serious attempt to explore in a systematic way the operation of a δ-crowding effect in ^{31}P spectroscopy.

3. Derivatives of the Bicyclo[2.2.1]heptane System

Work on rigid ring systems done prior to the initiation of this research program[5] had revealed that an effect other than that of the well-known upfield shift of γ-substituents can play a role in establishing ^{31}P shifts. The effect is absent in non-polar phosphorus functions, which simply show upfield shifts when in the more crowded axial position of the rigid 4-t-butylcyclohexyl system:

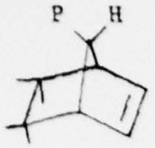
P = PH_2, $\delta^{31}P$ = -131.3 -111.6
PMe_2 - 45.8 - 42.5

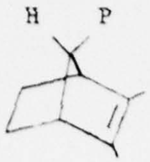
The effect can be present in functions that can be described as having P in relatively positive condition through inductive effects or ionic character:

P =	axial P	equatorial P
PCl_2	+208.9	+194.6
$P(OMe)_2$	+192.6	+190.0
$PSMe_2$	+ 43.3	+ 42.5
$\overset{+}{P}Me_3$	+ 30.8	+ 29.6

In this group of compounds, the least sterically crowded phosphorus (in the equatorial position) has the most upfield signal. Still, ^{13}C NMR shows that for the entire family of six phosphorus substituents steric crowding is present at C-3,5 in the axial isomer.

The question of whether steric crowding can cause the expected upfield shifts of ^{31}P in the polar-type substituent was clearly answered in the present program by our synthesis of several 7-substituted norbornane derivatives. This work has now been published[6]. In the anti position, corwding is much like that in the axial cyclohexyl position, but in the syn position, crowding is minimized. For three polar phosphorus substituents, the relief of crowding did indeed cause a downfield shift:

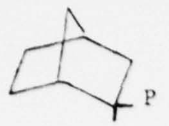




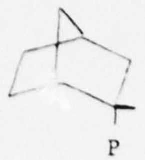
P =	anti	syn
PCl_2	+190.9	+199.7
$P(S)Me_2$	+ 30.2	+ 36.5
$\overset{+}{P}Me_3$	+ 19.8	+ 24.2

We view this result as being quite significant; no other new bond interactions at the α and β positions developed in the shift to the syn position, whereas definite changes do occur in moving from axial to equatorial on cyclohexane rings. Therefore, we propose, as one possibility, that the increase in gauche C-H bonds of the latter (at C-2,6) may be responsible for a shielding effect that is greater even than the shielding due to steric compression from C-3,5 in the axial position. For the Me_2P group on the norbornene system, a slight shielding effect was observed on going from anti (-60.2) to syn (-61.3), which may be the result of the well-known anisotropic effect of the double bond. Presumably this effect operates on the other P functions as well, but is more than counter-balanced by the relief of strain of these larger groups. Interesting also in these data is the generally high-field location of all ^{31}P signals, a result of the bond angle contraction at C-7 which is also felt on $^{13}CH_3$ when at this position. Presumably s-character is diverted into the exocyclic sigma bond.

This new thought of a shielding influence from an increase in gauche CH bonds can be put in broader terms using dihedral angle relations: in two related structures, greater shielding of P will be experienced in that structure with the smaller dihedral angles to β-CH bonds. To test this generality, we then prepared a series of 2-norbornyl derivatives, with the results below.
A manuscript describing this work has been submitted for publication[7].



exo



endo

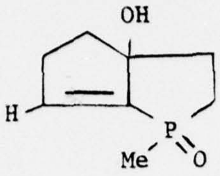
P=			Δδ
PCl_2	+187.5	+196.8	+9.3
PClBr	+183.9	+191.3	+7.4
$P(OMe)_2$	+185.3	+192.4	+7.1
$PO(OMe)_2$	+ 35.6	+ 36.8	+1.2
$\overset{+}{P}Me_3$	+ 30.1	+ 29.5	-0.6
$POMe_2$	+ 45.6	+ 44.5	-1.2
$PSMe_2$	+ 42.9	+ 40.2	-2.7
PMe_2	- 43.2	- 47.4	-4.2

The first four compounds have the exo signal upfield of the endo; this is the same unexpected result as seen in the cyclohexanes, since exo is less crowded than endo. The second four have the opposite relation, a result of the steric crowding in the endo position, although some of the values differ but little. Unlike the change at the 7-position, a definite difference in the dihedral angle between C-P and a β-CH bond does exist at the 2-position; we have calculated from published[8] X-ray data for another type of norbornane that the proton on C-1 has a dihedral angle of 39.0° for an exo-2 substituent but 84.2° for an endo-2. It appears, then, that two effects are operating in this cyclic system, just as in the cyclohexane system; steric crowding by γ-related C-6 causes the usual upfield shift for the endo position (as is well-known for $^{13}CH_3$), but another effect (our proposed β-CH effect from C-1) can cause almost as much or more shielding in the exo position. Again, this effect is largest for certain polar groups, and minimal for the non-polar Me_2P group.

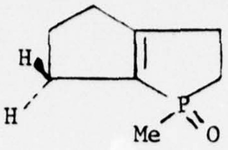
We therefore have a working hypothesis which seems to explain the peculiar results of changes in steric environment on ^{31}P shifts. A basis in theory will now be sought to explain the nature of the proposed β-CH interaction with phosphorus. This receives mention in Section III, Theoretical Program. Our relation will continue to receive experimental testing, however.

Two pieces of unrelated ^{31}P information[9] do become understandable on the basis of this hypothesis.

(1)



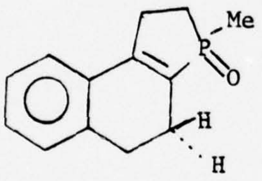
12, +32.0



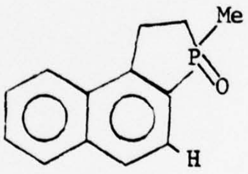
13, +63.2

The value for 12 is the most upfield we believe ever to be recorded for a phospholane oxide derivative, which are always unique in having especially deshielded phosphorus. The value for 13 is typical. The hydroxy group of 12 is not responsible for this effect, for we have made many alcoholic derivatives of the 5-membered system and find no such shielding effect. Nor does an explanation emerge from d-p π-bonding arguments, since the same structural feature is present in both substances. We propose that the eclipsing provided by the β-CH that is olefinic in 12 causes the pronounced upfield shift. In the model 13, the P atom lies between two β-CH bonds, hence by larger dihedral angles, and no unusual modification of the environment about P prevails.

(2)



14, δ^{31}P = +65.1



15, +56.1

Again, changes in π-orbital interaction seem less able to explain the upfield shift on aromatization of the central ring than does eclipsing by the β-CH bond of 15. In 14, P again falls between two β-CH bonds. This is the explanation for the shift effects in phenanthrenes 9 and 10, to which reference was made in part 2. Several other examples of the aromatization effect have been noted[4]; it holds also for phosphines, which would be even less involved in π-orbital interaction than phosphine oxides and hence more confidently to be associated with the β-CH effect (although our experience with norbornanes and cyclohexanes so far shows that phosphines generally have a weak response to this effect).

^{13}C NMR spectra have been recorded on the various norbornyl derivatives; of particular note is the considerable variation in 3-bond $^{13}C-^{31}P$ coupling. Others have noted for the phosphonate (e.g., ref. 10) and phosphine oxide[11] groups that the magnitude of this coupling is controlled by the dihedral angle relating the coupled atoms. Our work on the present project, soon to be published[7], clearly shows that similar plots, with coupling minima in the ϕ=90° region, exist for other P(IV) functions. Most importantly, however, is our observation that P(III) functions have minima at quite different dihedral angles (105°-110°)) the curve is quite asymmetric, with much larger coupling prevailing for ϕ=0° than ϕ=180°, and the best fit of the data makes use of a change in sign near the minimum. A sample plot (for $-PCl_2$) is provided as Fig. 1; pertinent ϕ and $^3J_{PC}$ values derived from our work are given in Table 1.

Fig. 1. Relation of $^3J_{PC}$ and Dihedral Angle

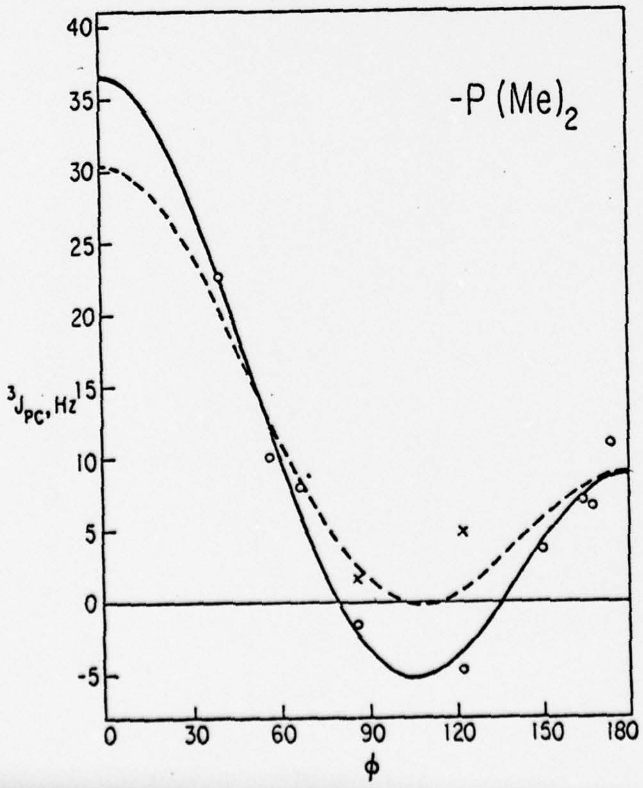


Table I. Dihedral Angles and Absolute Three-Bond Coupling Constants[a] for Various Phosphorus Functions

φ°	$PO(OMe)_2$	$P(O)Me_2$	$PSMe_2$	$\overset{+}{P}Me_3$	PCl_2	PMe_2	$P(OMe)_2$
40[b]	5.4	6.2	6.6	7.1	26.9	22.7	24.0
57[c]	-	-	-	-	10.4	10	-
67[d]	-	-	4	4	9	8	7
86[e]	0	0	0	0	4.7	1.8	-
122[f]	3.9	3.1	3.6	3.2	0	4.4	-
120[g]	-	-	4.8	-	-	-	-
150[h]	19.5	13.5	13.4	15.3	3.6	3.6	3.0
164[i]	-	-	-	-	6.1	7	-
167[j]	18.3	14.7	14.6	14.7	8.0	6.6	7.5
174[k]	-	-	13	15	11	11	9

[a] For consistency, all values for 2-norbornanes are taken from the 15.0 MHz spectra. [b] C-6 in endo 2-norbornanes. [c] C-2,3 in 7-norbornanes.

[d] C-3,5 in cis-4-cyclohexanes. [e] C-7 in exo 2-norbornanes.

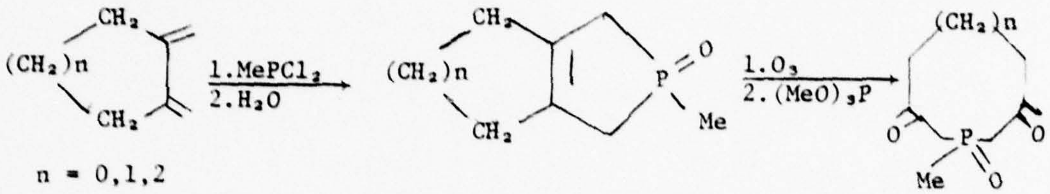
[f] C-4 in exo 2-norbornanes. [g] C-4 in endo-2-norbornanes.

[h] C-7 in endo 2-norbornanes. [i] C-5,6 in 7-norbornanes.

[j] C-6 in exo 2-norbornanes. [k] C-3,5 in trans-4-cyclohexanes.

4. Influence of Conformation of Large-Ring Compounds on ^{31}P Shifts

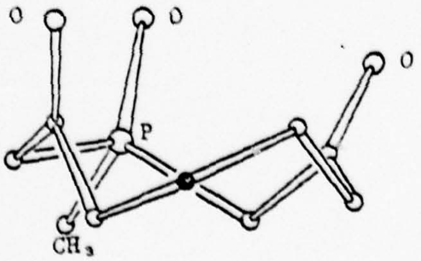
The following synthetic method was developed in another project in this laboratory[12]:



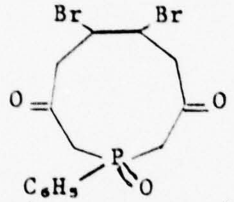
The products represent a new series of compounds, and indeed are among the very few phosphorus compounds known to have rings 7,8 or 9 members. The ^{31}P spectra were recorded during this work, and there was evident a notable, if not dramatic, deshielding effect in the 9-membered ring:

Ring size	δ^{31}P	∠ C-P-C
7	+29.8	105.0°
8	+29.0	106.1
9	+32.0	106.3

The effect is not related to bond angle differences, for we found through X-ray analysis (with the aid of Prof. A. T. McPhail and associates) that the 8- and 9-membered rings have virtually identical internal C-P-C angles. The shapes of the rings are drastically different, however; the 8-membered ring has C_2 symmetry with P on the C_2 axis in the chair-boat shape while the 9-membered ring has no symmetry elements, even though it adopts a modified twist-chair-chair conformation (shown below) with the unusual arrangement of the three oxygen atoms on the same face of the molecule.



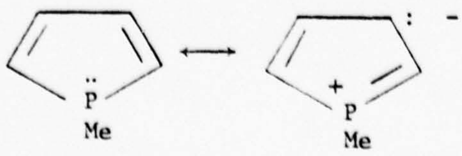
The small ^{31}P shift difference must rise from different non-bonded interactions in the two ring systems. The asymmetry in the crystal does not persist in solution, however, for spectral studies show, e.g., no difference in the C=O signals by ^{13}C NMR, and apparently a conformational interconversion is taking place. Another derivative of this ring system has been made which does retain the lack of symmetry in solution, however. The dibromide below has two C=O ^{13}C NMR signals (as it does for other carbons) with slightly different C-P coupling constants [δ 201.3(J=3.9) and 199.8(J=6.8)]



This remarkable observation suggests that the barrier to ring interconversion ($\Delta G^{\neq}$) is around 20 kcal/mol. It now becomes of interest to determine ^{31}P NMR shifts of such "stiff" rings, and to explore the conformational effects produced by elevation of temperature, and by ring substituents on ^{31}P shifts. Numerous other aspects of these rings call for study, and some are further discussed in the section on Proposed Research. Our data so far are of interest in pointing out a whole new area of cyclic phosphorus chemistry which can give information on ^{31}P NMR shifts just as smaller (5 and 6) membered rings have in our earlier work.

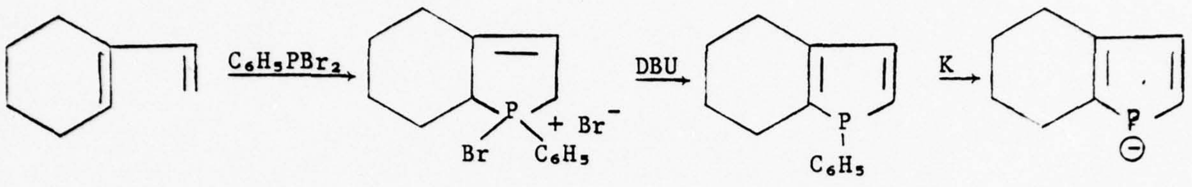
5. ^{31}P Effects in Phosphole Anions and Dimeric Phosphole Derivatives

The importance of electron delocalization from trivalent phosphorus into a π-system and its relevance to ^{31}P chemical shifts remains a matter for debate. We have previously used this concept to explain pronounced downfield ^{31}P shifts in phospholes[13] and 2-phospholenes[14] relative to their saturated (phospholane) counterparts:

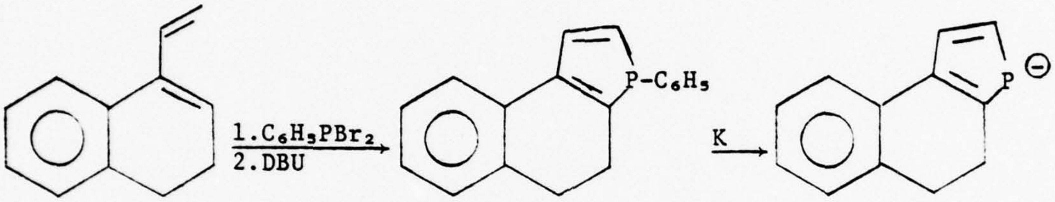


etc.

We reasoned that the effect should be far more pronounced with an exceedingly electron-rich phosphide anion, and during the present research program we explored this possibility by preparing the new phospholes and their anions below.

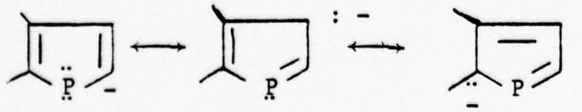


$\delta^{31}P = +10.5$ $\delta^{31}P = +73.3$



$\delta^{31}P = +12.5$ $\delta^{31}P = +81.7$

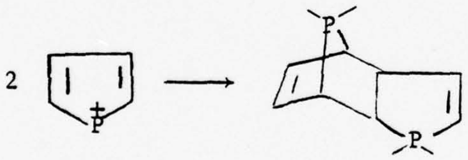
Such multicyclic phospholes have proved to be much easier to handle than monocyclic species. The cleavage of phenyl to form the anions proceeded in high yield to give stable solutions (THF) whose ^{31}P NMR were measured. The results were astonishing; both anions were in the same range, far downfield of any previously recorded anion of a secondary phosphine, which are usually upfield of phosphoric acid. We believe this may be attributable to delocalization of the form below which gives considerable double-bond character to the divalent phosphorus atom.



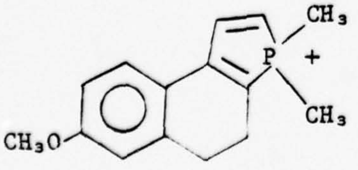
etc.

This symbolism would then suggest greater "aromaticity" for the electron-rich phosphole anions than for the phospholes themselves, a point already predicted by a theoretical study[15]. Our work in this area is quite incomplete at this writing, but it has considerable significance in our study of structural effects on ^{31}P shifts and will be continued.

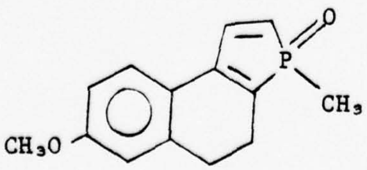
Another striking observation has come from a study of the dimers[16] of certain phosphole oxides (which form immediately on oxidation of the monomeric phospholes) or of phospholium ions (which form slowly from the monomeric ion). While we have examined the latter structures in earlier work[16a], our ^{31}P NMR measurements were made with more primitive instrumentation than we now have available, and we have observed two new features of considerable importance. With respect to the generalized structure below, which ignores the problem of which isomer structure is formed (only *one* is in fact formed), we now find that (1) the two phosphorus atoms have extremely different chemical shifts, as has been reported for the oxides[16b], one being in the expected region for the 2-phospholene structure, the other being at extraordinarily *low* field, (2) the ^{31}P nuclei *couple* with each other through three bonds, giving on the spectrum a total of four signals.



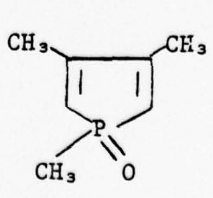
Thus, for the dimer of phospholium salt 16, one doublet appears at +52.6 ($^3J_{PP}$ = 44 Hz), the other at +96.1(J = 44); for the dimer of oxide 17, doublets (35 Hz) were at +56.4 and +88.3, while for the dimer of oxide 18, doublets (40 Hz) were at +56.8 and +79.0.



16



17



18

These are among the most downfield signals for a quaternary phosphonium salt ever recorded. These fascinating results must mean that the unique position of phosphorus in the bridge produces strong deshielding, either through exposure to long-range anisotropic effects or because of marked modificiations of bond and torsion angles. Examples of three-bond P-P coupling are obscure in the literature. We believe our results are the first ever recorded for phosphorus in the oxide and salt state, although King[17] has recorded some values for acyclic phosphines. It may well be that $^3J_{PP}$ is controlled by dihedral angle (Karplus) relations, again variable with P functionality just as we observed with $^3J_{CP}$. To the extent that the portion of the dimer molecules that possesses the bridging P atom resembles the norbornane system (with P at the 7-position), and with the other ring fused endo (as shown for dimeric phosphinates by Lipscomb[18]), then the dihedral angle relating the two P atoms is about 150°. This unique geometrical feature of our molecules may be responsible for the large ^3J values we observe; construction of systems with other dihedral angles will certainly be of interest.

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III. Theoretical Program

The basic goals of the theoretical part of our research have been to reproduce the ^{31}P chemical shifts in a variety of phosphorus-containing compounds and to understand the observed (and calculated) shifts in terms of basic chemical structure parameters. Since the accurate calculation of second order properties by quantum mechanical techniques still remains a difficult problem, an additional and more general goal of our work is to understand and reproduce theoretically chemical shifts in general. Our initial approach to this problem--and that which we propose to continue in further work--is a two-fold one·employing both semi-empirical and ab initio methods. Ideally, the ab initio approach is best in that it is theoretically rigorous and in the limit of the best possible calculations must reproduce experimental results exactly. It is, however, slow and difficult practically because of the current limitations on our ability to do the "best possible calculations". The fact that by suitable approximations significant progress is being made in this area does encourage us to maintain this approach. Semi-empirical approaches are sometimes difficult to justify theoretically but are much easier computationally, much faster to perform and, a not insigificant facet of their useability, they are easy for others to use once established. A flaw of which one must be clearly aware is the fact that a theory parameterized to correctly reproduce physical observable A may yield results for observable B which are incorrect. This potential problem is particularly important for the current work since we wish not only to reproduce phosphorus chemical shifts (property A) but also wish to correlate them with things such as charge distribution, overlap populations, and molecular geometry (properties B). We do believe, however, in the utility of semi-empirical theories and believe that our two-fold approach allows each method to compliment and restrain the other in the search for physical understanding of these systems. As our theoretical machinery is properly developed we will be able to apply it to the specific phosphorus systems of interest as well as more general chemical problems.

As an ab initio method we have chosen to employ the gaussian-70 program developed by Pople and co-workers[1]. Our attention initially was drawn to the success of Ditchfield[2] in employing this method coupled with the so-called gauge invariant atomic orbital (GIAO) approach. A current problem with calculations involving vector potentials is that of choice of gauge. In particular, the choice of origin of the coordinate system affects the gauge and, unless a mathematically complete calculation is carried out, will lead to an origin-dependence of the results. Since complete calculations are not generally possible for most molecular systems, this remains one of the more frustrating problems in the general calculation of second order properties. London[3] showed that by replacing the orbital $\phi_i(r)$ located at $\vec{R}_n$ by

$$e^{-(ie/\hbar c)\vec{A}(\vec{R}_n)\cdot\vec{r}}$$

the dependence on choice of origin within a particular basis set (see the discussion by Epstein[4]) could be removed. Ditchfield employed such orbitals in his Hartree-Fock approach (we propose to call such orbitals London orbitals) and was able to obtain relatively good (certainly improved over existing theoretical calculations) results for a series of different nuclei in small molecules. We have obtained copies of the gaussian-70 program from both Professors R. G. Parr of the University of North Carolina and W. L. Luken of this Department and have initiated the necessary modifications of these programs to perform chemical shift calculations. Certain new integrals involving angular momentum operators must be evaluated in the gaussian basis sets and a perturbed SCF procedure must be written which can handle the general case of variable bases in SCF MO calculations[5].

The current status of the program is that the calculations of the diamagnetic contributions to the chemical shift have been written and tested, but the paramagnetic terms are only partially operational. As Table I shows, we are able to reproduce the diamagnetic component of the chemical shift for a variety of molecules at the same level of basis set as others.[6] Table I shows an additional confirmation of the correctness of the diamagnetic calculations as it demonstrates the fact that the diamagnetic contribution to the chemical shift is a minimum (for any particular atom) when the electronic centroid (for the symmetric molecules shown this corresponds to the center of mass) is chosen as origin.[7]

The overall program has also been modified for improved efficiency. Calculations of this type are of necessity lengthy and require extensive computer storage. For example, calculation of the carbon chemical shift on the small molecule CH_4 requires about 1.5 minutes while for allene nearly 8 minutes of computer time are needed. The requirements of the larger and physically more interesting molecules will clearly be very much greater. At the moment the storage requirements of the program have been reduced from 398 to 358 Kbytes, and we believe additional reductions in running time are possible.

Since our ab initio calculation is based on a SCF procedure we chose as a semi-empirical approach to focus on first the CNDO method.[8] Looking ahead to the possibility of performing some configuration interaction (CI) calculations, we chose the CNDO/S modification by Jaffe and Del Bene[9] for this work. The S version of the CNDO procedure is modified to include a semi-empirical coulomb integral evaluation as well as a differentiation of the sigma and pi type resonance integrals; in particular, it has been parameterized in order to give a good fit to optical spectra of organic molecules. In a CI-type calculation one would clearly want good excitation energies. The more recent version is due to Ellis, Kuehnlenz and Jaffe[10] in which the Nishimoto-Mataga approximation[11] to the coulomb repulsion

Table I

A comparison of σ_{dia} (in ppm) for carbon in some representative molecules for a guassian-70 type calculation in a 4-31 basis.

molecule	DMP[a]	this work	this work
	origin = c. m.		origin = carbon atom
CH_4	296.2	296.0	296.0
C_2H_2	301.9	301.6	354.5
C_2H_4	311.7	310.4	329.2
C_2H_6	320.8	320.2	336.9
(CH_2CCH_2)[b]	365.1	365.7	365.9[d]
(CH_2CCH_2)[c]	304.3	305.2	348.4

a. R. Ditchfield, D. P. Miller, and J. A. Pople, J. Chem. Phys. 54, 4186 (1971).

b. Shift is for central carbon atom.

c. Shift is for terminal carbon atom.

d. Origin = terminal carbon atom.

integrals has been employed. In addition, the d-orbital package from our original CNDO/2 program has been incorporated. A perturbed Hartree-Fock treatment was added to the program using the London-orbital basis and the CNDO approximations in the calculation of chemical shifts as outlined earlier by Pople.[12] The dipolar approximation was employed and tested by comparing calculations to exact formulas for certain angular momentum integrals; we find in nearly all cases the dipolar approximation at normal bond distances to be quite adequate.

First calculations using this program of chemical shift parameters yielded very poor results. For example, a representative five-carbon-compound set (see Table II) showed a disparity between the experimentally observed and calculated chemical shifts from our initial program of almost 50 ppm on the average on an absolute scale and better than 20 ppm on a relative scale. Comparison of calculated and observed chemical shifts for other species and other varieties of carbon compounds showed similar poor agreement.

Semi-empirical theories are parameterized to do the best they can for as many properties of interest as possible. Ellis, Maciel, and McIver[13] were successful in reparameterizing their INDO perturbed Hartree-Fock theory to suitably reproduce ^{13}C chemical shifts among a reasonably wide range of chemical situations. This work has been extended to fluorine substituted hydrocarbons[14] and also nitrogen-containing compounds.[15] Since our original calculations were relatively poor, we were interested to see whether our modified CNDO/S procedure could also be reparameterized successfully along the same lines. In order to do this we carried out a number of calculations on the carbon compounds indicated in Table II to compare the experimentally determined ^{13}C chemical shift with that which we could calculate. These compounds were chosen because they are relatively simple, incorporate a number of features of general interest in hydrocarbon chemistry, and, most importantly, because they span a wide range of observed ^{13}C chemical shifts.

In CNDO calculations the variable parameters include the resonance parameters (β_o) for each atom and the parameters (I + A) for each type of shell (s or p or d) for each type of atom. Accordingly, for carbon-hydrogen compounds one has five parameters to vary and in principle must search a five-dimensional hyperspace in order to find optimum agreement with experiment. Since such a procedure is obviously time-consuming and costly our original attention was focused on maintaining the hydrogen parameters as they currently exist in the S program (for hydrogen, $\beta_o = -12.0$ eV and $(I + A) = 14.35$ eV), and to require that the changes in the I + A parameters for the carbon s and p shells be the same. Thus, we have performed a simple grid search in a two-dimensional hyperspace using a small subset of "calibrating" molecules with the results shown in Table II.

The calculations are valence shell calculations with an inner shell diamagnetic contribution determined separately and added in. Three sets of calibrating molecules were used to search for a best fit. The set C2 consisted of the full complement of methane, ethane, acetylene, ethylene, and allene (central carbon) while set C1 did not employ methane and set C3 did not use allene. Since a best fit is being attempted, the data once calculated were least-squared adjusted to give the best mean fit to the experimental data; the parameter $\bar{x}$ appearing in the table represents this additive correction for each overall set of calculations. In the table we present data for the calibrating sets by themselves (C1, C2 and C3) as well as the full 14-carbon-nucleus calculation. The three calibrating sets lead to essentially two points in the parameter space so that only two calculations on the full 14-carbon-nucleus set are shown. For purposes of comparison, the data of Ellis, Maciel and McIver[13] are also included in the table calculated on the same bases.

Several comments can be made with regard to the results in Table 2. First of all, the perhaps more reasonable calibrating set C1 (since it spans a greater range of chemical shift) leads to very good results in our calculations for the calibrating set, but when this calibration is applied to the full complement of molecules and compared to the result obtained by Ellis, Maciel and McIver (EMM) somewhat poorer agreement is obtained. Using the full 5-molecule calibrating set or eliminating allene from the set does not significantly change the results. Overall, the general agreement between the results here and those of EMM is close; EMM's calculations give somewhat better overall trends than does our own best set, S1. There are some obviously bad cases in all the calculations; in S1, methane, the central carbon of propane, and the terminal carbon in allene have quite large deviations from the experimental results.

The original β, U_{ss}, and U_{pp} carbon parameters from the CNDO/S program were -17.5, 29.9, and 11.6 eV, represpectively. As the results in the table indicate, the two optimum fit parameter sets turn out to be -22.5, 29.0, and 10.7 eV (S1) and -21.5, 32.0, and 13.7 eV (S2). The surface in the general region of these points was briefly investigated, and it was seen that the calculations are very sensitive to variation of β but only rather weakly dependent on the U_{ss} and U_{pp} parameters. This suggests that a more efficient procedure for parameter determination in a general N-type-atom problem might be to search the N-dimensional β-parameters subspace for extrema, keeping the U-parameter set fixed.

Since Ellis, Maciel, and McIver[13] do not report their search routine, we decided to attempt to reproduce their carbon INDO calculations and, indeed, see if they could be improved. Having recently become aware of the SIMPLEX optimization procedure[16] we used EMM's parameters as a starting point and have carried out a five-dimensional (a 6-vertex simplex) search for optimization, again using the five-molecule calibrating set of methane, ethane, acetylene, ethylene, and the central carbon of allene. Our first attempt employing this procedure has yielded improved results as shown in Table III. Because we are currently in the

Table II

Comparison of theoretical carbon chemical shifts for several calibrated CNDO/S calculations.

	σ_{exp}[1]	$(\sigma_{CALC} + \overline{X} - \sigma_{obs})$						
		S1	C1[2]	S2	C2[3]	C3[3]	EMM[4]	C4
CH_4	196.0	-21.8		-13.8	-9.0	-9.8	- 6.5	-2.7
C_2H_6	188.0	1.3	2.0	7.3	12.1	11.3	- 1.5	2.3
$H_3\overline{C}CH_2CH_3$	178.3	9.2		14.8			4.7	
$H_3C\overline{CH}_2CH_3$	177.8	26.6		30.8			8.9	
$H_3\overline{C}CH=CH_2$	173.4	10.7		14.8			10.1	
$H_3CC\equiv\overline{C}H$	123.9	-11.6		-12.6			-13.1	
C_2H_2	120.0	- 3.6	-2.9	- 5.4	-0.6	-1.4	-11.1	-7.3
$H_2\overline{C}=C=CH_2$	119.2	-25.8		-24.1			-18.4	
$H_3C\overline{C}\equiv CH$	108.2	7.7		4.5			-11.1	
$H_3CCH=\overline{C}H_2$	77.4	- 9.6		-11.2			- 0.1	
C_2H_4	70.6	- 1.7	-1.0	- 4.0	0.8	0.0	3.8	7.6
C_6H_6	65.2	2.5		- 3.4			3.6	
$H_3C\overline{CH}=CH_2$	58.1	15.2		10.0			5.1	
$H_2C=\overline{C}=CH_2$	-18.8	1.3	2.0	- 8.2	-3.4		25.6	
std. dev.		14.1	2.4	14.5	7.8	8.7	11.5	6.4
$\overline{X}$		-24.0		-18.8			-19.0	

[1] Experimental data tabulated by B. R. Appleman and B. P. Dailey (Adv. in Mag. Res. 7, 231 (1974)) and that of Ellis, Maciel, and McIver (ref. 13) referred to the ^{13}C absolute scale for which $\sigma(CO) = +12.0$.

[2] $U^c_{ss} = 29.0$, $U^c_{pp} = 10.7$, $\beta^c = -22.5$ eV.

[3] $U^c_{ss} = 32.0$, $U^c_{pp} = 13.7$, $\beta^c = -21.5$ eV.

[4] See reference 13.

Table III

Comparison of Theoretical Carbon Chemical Shifts for a Partially Optimized SIMPLEX Treatment of the INDO Method

		$\sigma_{CALC} + \overline{X} - \sigma_{obs}$		
	σ_{exp}[1]	SO[2]	SO/CS	EMM[3]
CH_4	196.0	- 4.3	-2.2	- 6.5
C_2H_6	188.0	2.2	4.3	- 1.5
$H_3\overline{C}CH_2CH_3$	178.3	8.0		4.7
$H_3C\overline{C}CH_2CH_3$	177.8	11.9		8.9
$H_3\overline{C}CH=CH_2$	173.4	10.7		10.1
$H_3CC\equiv\overline{C}H$	123.9	- 6.8		-13.1
C_2H_2	120.0	- 3.0	-0.9	-11.1
$H_2\overline{C}=C=CH_2$	119.2	12.7		-18.4
$H_3C\overline{C}\ CH$	108.2	- 2.7		-11.1
$H_3CCH=\overline{C}H_2$	77.4	-12.6		- 0.1
C_2H_4	70.6	- 3.3	-1.2	3.8
C_6H_6	65.2	-10.6		3.6
$H_3C\overline{C}H=CH_2$	58.1	- 0.4		5.1
$H_2C=\overline{C}=CH_2$	-18.8	- 1.9	0.2	25.6
stand. dev.		8.1	2.5	11.5
$\overline{X}$		8.1		-19.0

[1] See reference 1 of Table II.

[2] Simplex optimized differences for full molecular set (SO) and calibrating set SO/CS. Optimized parameters are: $U^{C}_{ss} = 32.91$, $U^{C}_{pp} = 13.31$, $\beta^{C} = -16.26$, $U^{H}_{ss} = 14.95$, $\beta^{H} = -12.6$, all in eV.

[3] See reference 13.

midst of these calculations, we report on what is probably only a partially optimized parameter set; however, the improvement in the calculated carbon chemical shifts is notable.

The five-molecule calibrating set yields very good answers and, in contrast to our earlier CNDO/S calculations, re-orders methane and ethane properly. Calculation of the full 14-carbon-nucleus set shows an overall reduction in the standard deviation relative to EMM's results of 11.5 to 8.5. The ability to calculate the shift of the central carbon of allene much better is a significant factor in the improvement.

We are encouraged by the success of this method as applied to carbon and, indeed, feel that not only can it be applied to phosphorus shifts but also that it can lead to significant improvements in parameterization of other nuclei.

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IV. APPENDIX

A. Publication Resulting from the Grant

1. Courtland Symmes, Jr. and Louis D. Quin, "Phosphorus Nuclear Magnetic Resonance Spectra of Complexes of Aluminum Chloride with Phosphorus (III) Chlorides: Structure of the Reaction Product from the Phenylphosphonous Dichloride Complex with Tetramethylethylene," J. Org. Chem., 43, 1250 (1978).

2. Louis D. Quin and Lory B. Littlefield, "Importance of the Structure of the Phosphorus Functionality in Allowing Dihedral Angle Control of Vicinal ^{13}C-^{31}P Coupling. Carbon-13 NMR Spectra of 7-Substituted Bicyclo[2.2.1]-heptane Derivatives," J. Org. Chem., 43, 3508 (1978).

3. L. B. Littlefield and L. D. Quin, "Comparison of Steric Effects on ^{31}P Chemical Shifts in Some 7-Norbornyl, 7-Norbornenyl, and Cyclohexyl Phosphorus Compounds," Org. Magnetic Resonance, 12, 199 (1979).

4. W. L. Orton, K. A. Mesch, and L. D. Quin, "Synthesis and ^{31}P NMR Study of Dihydronaphthaleno- and Naphthaleno- Derivatives of Phospholene Oxides," Phosphorus and Sulfur, 5, 349 (1979).

5. L. D. Quin and W. L. Orton, "Evidence for Delocalization in Phosphole Anions from their ^{31}P NMR Spectra," J. Chem. Soc. Chem. Comm., 401 (1979).

6. L. D. Quin and K. A. Mesch, "Three-Bond ^{31}P-^{31}P Coupling in Dimers of Phospholium Salts and Phosphole Oxides," Org. Magnetic Resonance, 12, 442 (1979).

7. L. D. Quin, M. J. Gallagher, G. Cunkle and D. B. Chesnut, "^{31}P and ^{13}C NMR Studies of 2-Norbornylphosphorus Compounds Karplus Equations for $^{3}J_{PC}$ in Several p(III) and p(IV) Derivatives," J. Am. Chem. Soc., submitted.

8. D. B. Chesnut and F. W. Whitehurst, "A Simplex Optimized INDO Calculation of ^{13}C Chemical Shifts in Hydrocarbons," J. Comput. Chem., submitted.

B. List of Persons Who Worked on ARO Grant

Undergraduate Students

Glen Cunkle

Graduate Students

Frederick Whitehurst
William Orton
Keith Mesch
Eric Middlemas
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