Heteroatom Chemistry
Volume 8, Number 5, 1997

The Characterization of NMR Shielding in Monocyclic Phosphines

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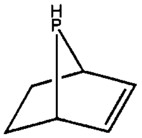
Received 26 February 1997

ABSTRACT

The phenyl-substituted saturated monocyclic phosphines, PhP(CH$_2$)$_n$, n = 2–5, show an interesting variation in their phosphorus NMR shieldings. The shielding does not vary uniformly with ring size, but rather the smallest ring (n = 2) has the highest shielding while the next smallest (n = 3) has the lowest shielding. Hartree–Fock calculations in the gauge-including atomic orbital (GIAO) approach on the related hydrogen derivatives have reproduced this trend in shielding and allow a qualitative understanding of the experimental observations. With respect to the relatively unstrained n = 4,5 ring systems, the unusual behavior of the n = 2 and 3 molecules can be understood in terms of the differences in the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) gaps and the p-character of the phosphorus lone pair. The HOMO/LUMO gap is largest for phosphirane (n = 2) but smallest in phosphetane (n = 3). The hybrid character of the lone pair in phosphirane (n = 2) is almost sp while that for phosphetane (n = 3) is essentially sp^2. © 1997 John Wiley & Sons, Inc. Heteroatom Chem 8*: 451–457, 1997*

INTRODUCTION

Structure features are well known to exert strong influences on the ^{31}P NMR shift of cyclic phosphines, but explanations for the observed shift changes even among related compounds are not always apparent. We have recently made progress in the interpretation of ^{31}P NMR shifts of some complex phosphines (the bridged 7-phosphanorbornene (**1**) [1] and the fully unsaturated phosphole (**2**) [2] systems) by using an ab initio quantum-mechanical approach, and we have now turned our attention to the case of the saturated monocyclic phosphines. Even in this simple family, uncharacterized influences are present that cause, for the members with 3–6 ring atoms, a spread of about 250 ppm in chemical shift. Much of the literature has been reviewed by Gallagher [3], who points out clearly the lack of understanding of this phenomenon. The family of P-phenyl substituted monocyclic phosphines PhP(CH$_2$)$_n$, recently completed with the first synthesis of 1-phenylphosphetane [4], admirably reveals the ^{31}P shift anomaly as the ring size increases. Thus, 1-phenylphosphirane (n = 2) has the most upfield shift (δ − 236 [4]),



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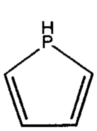

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Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

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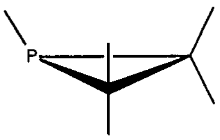
CCC 1042-7163/97/050451-07

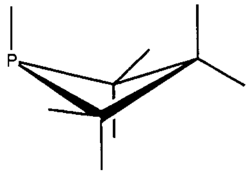
while inserting one carbon to form 1-phenylphosphetane ($n = 3$) leads to the most downfield shift ($\delta + 13.9$ [4]); the shift moves back upfield in 1-phenylphospholane ($n = 4, \delta - 15.3$ [5]) and farther upfield in 1-phenylphosphinane ($n = 5, \delta - 34.3$ [6]). Clearly there is no simple correlation of the bond angles at phosphorus with this effect. The very strong shielding in the phosphiranes has been attributed to the high *s*-character of the lone pair on phosphorus, the argument being that in this orbital the lone pair is close to the ^{31}P nucleus [7]. But such an explanation fails to account for the huge downfield shift (250 ppm) merely on insertion of one carbon into the ring, nor for the further shielding as other carbons are added, and we do not believe it applicable for all ring sizes.

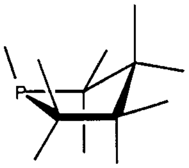
In the present study, we employ ab initio quantum-mechanical calculations on the hydrogen derivatives (as opposed to the phenyl derivatives) to derive an understanding of the shift effects in the cyclic phosphines. We are able to reproduce the trend of the shifts, and analysis of the wave functions involved provide a good qualitative understanding of the phenomena.

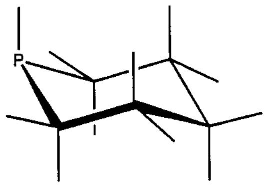
DETAILS OF THE CALCULATIONS

The molecules studied in this investigation included the saturated monocyclic phosphines, $HP(CH_2)_n$, with ring sizes ranging from 3 to 6: $n = 2$, phosphirane; $n = 3$, phosphetane; $n = 4$, phospholane; $n = 5$, phosphinane (see drawings below).









The hydrogen derivatives rather than the phenyl derivatives (for which experimental shifts exist) were studied because the latter molecules would be too central-processing-unit (CPU) expensive. The structures were optimized at the MP2/6-31G(*d*) level [8] with energies calculated at the MP2/6-311G(*d,p*) level; the frozen core approximation was employed along with sets of six *d* polarization functions. The phosphorus basis set in the 6-311G(*d,p*) approach is the 12*s*9*p* basis of McLean and Chandler [9] in a [6*s*,5*p*] contraction. The NMR shielding calculations were carried out at the GIAO [10] RHF/6-311G(*d,p*) level with one set of polarization functions on hydrogen and carbon and two sets of *d* polarization functions on phosphorus, the latter a [6*s*,5*p*,2*d*] basis. The exponents of the phosphorus polarization functions were obtained by multiplying and dividing the standard exponents in the Gaussian 94 code [11] by 2, as suggested by Frisch et al. [12]. The highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) energy gaps were also determined from the basis sets used in the shielding calculations. All of the calculations used the Gaussian 94 program and were carried out on a Cray 916 computer located in the North Carolina Supercomputer Center.

Except as noted, chemical shieldings calculated here are reported as absolute values. While experimentalists tend to report relative displacements of the NMR lines (relative to some standard, which in the case of phosphorus is typically 85% phosphoric acid), normally called "chemical shifts," δ, theoretically one determines an "absolute" displacement, usually referred to as "chemical shielding," σ. The latter is really a shift with respect to the bare nucleus and is such that more positive values indicate diamagnetic or upfield shifts (more negative δ values), and more negative values indicate paramagnetic or downfield shifts (more positive δ values). Experimental shifts [4–6] have been converted to absolute shieldings using the absolute shielding for phosphoric acid that has been determined to be 328.4 ppm [13]. The advantage of absolute shifts is that systematic errors are not hidden by a relative comparison, and, of course, relative shifts, if desired, are easily obtained from the absolute values [14].

RESULTS AND DISCUSSION

Geometries and Energies

There are two possible structures for phosphetane ($n = 3$) and phosphinane ($n = 5$). For phosphetane, the pseudoaxial form is calculated to be lower in energy than the pseudoequatorial form by 1.32 kcal/mol [15]. The axial form of phosphinane is calculated to be more stable than the corresponding equatorial form by 2.29 kcal/mol. This is consistent with an experimental determination of the axial–equatorial ratio (9:1) in solution at room temperature [16]. The angle between the CPC and CCC planes in phosphetane was found to be 38.78° and is larger than those reported for this compound with bulkier substituents [17a]; the fact that it is calculated to be larger is also in disagreement with earlier predictions based on angle trends with size of substituent [18]. With the exception of phospholane ($n = 4$), the molecules studied here exhibit C_s symmetry. Phospholane has a twisted structure as shown in Figure 1 and has no symmetry (C_1 point group).

Table 1 shows some geometry details for the four molecules studied here. The PH distance is remarkably uniform throughout while the PC bonds (phosphorus and its adjacent carbons) have a standard deviation of only 0.011 Å. The CPC angles exhibit a steady progression from the extremely constrained $n = 2$ molecule with an angle of 47.0° to the relatively unstrained $n = 5$ system where the angle is 98.1°. One can also define the mean carbon position for those carbons adjacent to the phosphorus and from this derive an $HP\bar{C}_{adj}$ angle; the data in the table show that this latter angle is relatively insensitive to ring size, ranging from 95.6° to 100.7°. Generally speaking, our optimized geometries agree well with the data for such rings in more complicated structures [4b].

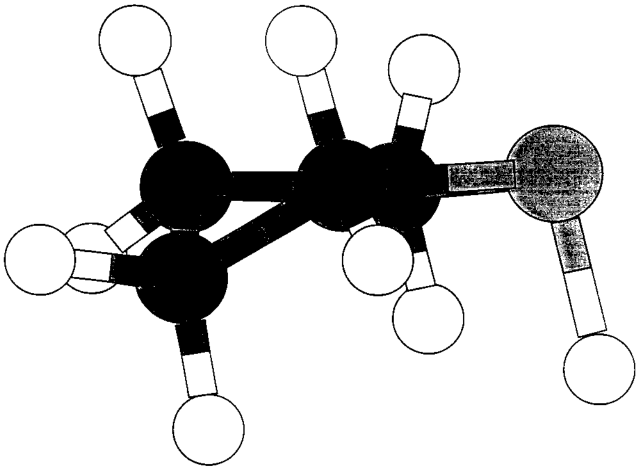


FIGURE 1 A drawing of the optimized phospholane ($n = 4$) molecule viewing the structure in a direction perpendicular to the plane formed by phosphorus and the two C_α carbons. One of the C_β atoms is +0.562 Å above the $C_\alpha PC'_\alpha$ plane, while the other C_β carbon is −0.101 Å below this plane. The two $C_\beta C_\alpha PC'_\alpha$ dihedral angles are 22.5° and 3.9°, respectively.

TABLE 1 Some details of the optimized geometries for the $HP(CH_2)_n$ monocyclic phosphines.

	Bond Lengths (Å)		Bond Angles (Degrees)	
n	*PC*	*PH*	*CPC*	$HP\bar{C}_{adj}$
2	1.869	1.417	46.97	95.62
3	1.888	1.422	74.51	96.04
4	1.877[a]	1.421	91.77	99.05
5	1.860	1.423	98.08	100.74

[a] Mean of 1.869 and 1.886 Å of the two nonequivalent PC bonds in this molecule.

Chemical Shieldings

The principal values, the isotropic shieldings, and the shielding ranges (the range is defined as the largest principal value minus the smallest principal value) are given in Table 2. Of the four molecules, all but the $n = 4$ case possess C_s symmetry so that one of the principal axes (here denoted as *zz*) will be perpendicular to this symmetry plane. Another principal axis (defined here as the *xx* principal axis) is in all cases approximately perpendicular (to within 10°) to the mean plane of the carbon atoms in each of the molecules; there is no symmetry requirement that this be so, and, of course, in the case of (the low-energy twisted form of) phospholane ($n = 4$), the molecule has no symmetry (C_1 point group). Accordingly, for this latter case the orientations of the three principal axes as described above are only approximate. The observed isotropic shieldings for phosphorus are also included in Table 2 and have been determined by using the observed δ values [4–6] and converting them to our absolute shielding scale where 85% phosphoric acid has a shielding of 328.4 ppm [13]. Data for the phosphorus proton and for the adjacent carbon atoms are also included in the table for completeness.

TABLE 2 NMR shieldings (ppm) for the monocyclic phosphines, $HP(CH_2)_n$. The principal values are given along with the range and the calculated and observed isotropic shieldings. These absolute shieldings may be changed to δ values using the absolute shielding of H_3PO_4 of 328.4 [13].

A. Phosphorus shieldings

n	σ_{xx}	σ_{yy}	σ_{zz}	*Range*	σ_{iso}^{calc}	σ_{iso}^{obs}
2	1059.8	478.7	513.1	581.1	683.8	564.4
3	236.7	473.4	437.1	236.7	382.4	314.5
4	360.1	481.8	451.8	121.7	431.2	343.7
5	440.0	429.9	391.8	48.2	420.6	362.7

B. Hydrogen and carbon shieldings

n	σ_{iso}^{calc}	$\sigma_{iso(C)}^{calc}$
2	32.73	195.7
3	27.97	175.5
4	29.20	175.0[a]
5	28.89	174.4

[a] The mean of 171.8 and 178.2 shieldings for the nonequivalent adjacent carbon atoms.

Comparison with Experiment

The data in Table 2 for the isotropic shielding are plotted in Figure 2 and show that our calculations for the hydrogen derivatives of the cyclic systems follows the observed trend very well for the shieldings that are observed for the phenyl derivatives. The mean difference of some 83 ppm may be attributed largely to the chemical-shift difference in the two derivatives, hydrogen versus phenyl. The replacement of hydrogen or methyl by phenyl typically leads to a downfield shift of some 110–120 ppm [19]. In addition, Hartree–Fock shieldings for phosphorus tend to be some 10–20 ppm high on average [20,21]. The relative ordering of the $n = 4$ and $n = 5$ cases is not reproduced theoretically, but this may be due to the difference in the two types of derivatives being compared as well as the fact that the observed differences in the shieldings for these two cases is of the order of the root mean square error with which phosphorus chemical shieldings can presently be calculated [20,21] (about 30 ppm) at the Hartree–Fock level. The calculated shielding range varies from a large 581 ppm in the $n = 2$ case to a small 48 ppm in the $n = 5$ molecule. The large range (and anisotropy) of phosphirane ($n = 2$) is very much like that seen in its silicon analog by Magyarfalvi and Pulay [22]. These authors showed that the very large shielding range seen in silacyclopropane is associated with the very small ring angle involving silicon.

It is also worth noting the shielding of the other nuclei in these systems. While the adjacent carbon resonance is rather high for the $n = 2$ case (such as it is for cyclopropane itself and related phosphorus ring structures [4b]), these carbon shieldings for the other members of the series vary very little. On the other hand, as shown in Figure 3, the trend in the phosphorus proton shielding exhibits a very close parallel to that of phosphorus itself, an effect that has not been reported experimentally. The ratio of the two shieldings is nearly constant (16 ± 3) and would seem to suggest that the mechanism responsible for the shielding variation of phosphorus is also involved in the proton shielding. Unfortunately, very little is presently known about the dominant contributions to shielding in hydrogen.

Although the difference in observed phosphorus shieldings in the larger, unstrained phospholane ($n = 4$) and phosphinane ($n = 5$) molecules is certainly experimentally significant, it is borderline in terms of the current theoretical noise level for phosphorus-shielding calculations. Certainly, the small (10.6 ppm) difference calculated for the hydrogen derivatives is likely not significant with the present theoretical capabilities. The difference between these two shieldings and that of the $n = 3$ (phosphetane) case should, however, be theoretically detectable, as obviously should the large deshielding in the $n = 2$ (phosphirane) molecule. What needs to be explained, then, is the very high shielding observed for phosphirane ($n = 2$) and the somewhat reduced shielding of phosphetane ($n = 3$). The differences in these two compounds from the others lie completely with the xx component of the shielding tensor, that component that is contained in the C_s symmetry plane and is approximately perpendicular to the mean carbon plane of the molecule. As can be seen from Table 2, this principal value has values of 360 and 440 ppm for the $n = 4$ and 5 cases, respectively, while it is a very large (shielded) 1060 for $n = 2$ and a rather low (deshielded) 237 in the $n = 3$ case. Generally speaking, the contributions to the diamagnetic

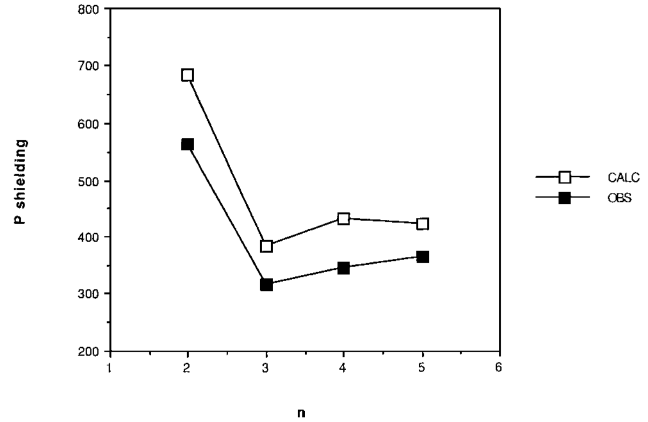


FIGURE 2 Absolute calculated (hydrogen derivatives) and observed (phenyl derivatives) phosphorus isotropic shieldings (ppm) for the monocyclic phosphines, $HP(CH_2)_n$, as a function of *n*.

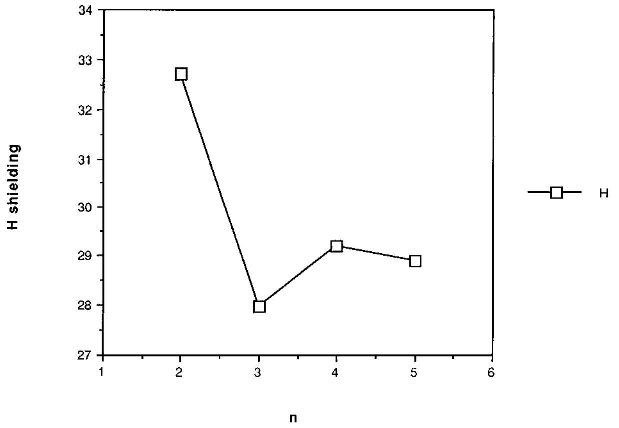


FIGURE 3 Absolute calculated phosphorus hydrogen isotropic shieldings (ppm) for the (hydrogen derivatives) monocyclic phosphines, $HP(CH_2)_n$, as a function of *n*.

shielding of most nuclei is relatively insensitive to molecular environment, the variation of NMR shielding coming about from the variation in the paramagnetic contribution. This is certainly true in the present study. The paramagnetic contribution in the case of phosphetane is more negative than for the other molecules involved, while for phosphorane it is actually positive, a most unusual situation. An analysis of the situation requires that we obtain some understanding for the big difference in these two cases.

The Origins of Chemical Shielding

Chemical shielding is caused by magnetic fields induced in the molecule by the application of an external magnetic field. Charge clouds are set in rotation as one turns on an external magnetic field, and the external field also tends to provide net currents in the molecule as the energies of electrons with equal and opposite angular momentum now differ . Contributions to the chemical shielding are usually divided into so-called diamagnetic and paramagnetic parts, an arbitrary but often useful division. It has been known for some time that the paramagnetic terms generally dominate changes in shielding for a particular (nonhydrogen) nucleus as its molecular environment is modified. As noted earlier, this is also true for the phosphorus species treated here.

The paramagnetic contribution comes about from the coupling of the external field term $(H \cdot L)$ between orbitals unoccupied in the Hartree–Fock ground state and those normally filled. The $H \cdot L$ operator acts like a rotation operator (dependent on the angular momentum quantum number) and will, for example, convert a p function pointing in the x direction into one pointing in the y direction when the external field is along the z-axis of the system. Strong paramagnetic effects are then to be expected when atomic orbitals have large coefficients in those molecular orbitals that are coupled by this operator . The more localized the molecular orbitals containing the rotationally related atomic orbitals tend to be, the larger will be the coupling. For example, one of the causes of the large paramagnetic shielding for double-bonded carbon is the localized nature of the p-π orbitals. Of special importance here is the localized nature of the phosphorus lone pair .

Because the theoretical approach involves perturbation theory, the coupling between molecular orbitals also depends upon the difference in orbital energies involved. Since basically one is coupling orbitals that are normally unoccupied with those that are normally occupied, one might expect that the smaller the HOMO–LUMO gap, the more likely strong paramagnetic shielding can be realized. Citing again the example of double-bonded carbon, the HOMO–LUMO gap in such systems is small because of the nature of π orbitals tending to lie at higher orbital energies as well as the π^* orbitals tending to lie at the lower-energy region of the unoccupied set. Indeed, this qualitative dependence upon the energy gap is the basis for the old average energy approximation used in shielding calculations over 35 years ago [23]. Because of its tendency to be nonbonding and therefore to lie toward the center of the HOMO–LUMO gap, the lone pair when present on phosphorus may be expected to be dominant in shielding variations of this nucleus as has been demonstrated previously in two important phosphorus systems [1,2].

The Case of the Monocyclic Phosphines

A careful and full analysis of the present situation would require access to the individual contributions, MO by MO, to the shielding in each molecule. Only by locating those major players in the shielding can one be sure of the analysis. Unfortunately, we do not currently have access to such a shielding decomposition routine and must, therefore, rely on some qualitative and semi-quantitative ideas. These ideas are, however, basic to NMR chemical shielding as discussed above and fit in well with the current results. There are basically two effects we wish to discuss: the HOMO–LUMO gap and the constitution in terms of s and p character of the lone pair orbital.

The HOMO–LUMO gap for the $n = 2$ case is the largest of all the four molecules studied here, while that of the $n = 3$ case is the smallest. These results are consistent with the $n = 2$ molecule being shielded and the $n = 4$ molecule deshielded relative to the other molecules in the series ($n = 4$ and $n = 5$).

Using our optimized geometries, we have recalculated the molecular orbitals in the small STO-3G basis in order to obtain a simple and ready analysis of the composition of the molecular orbitals. It is clear from these calculations that the HOMO orbital is dominated by the phosphorus lone pair and will be strongly coupled to the LUMO orbital that, on phosphorus, is represented by a p orbital perpendicular to the C_s symmetry plane. The paramagnetic term in the Hamiltonian will tend to rotate the lone pair orbital into conjunction with the p orbital that is perpendicular to the symmetry plane, as discussed earlier . The extent to which this coupling is effective in terms of giving rise to a deshielding effect will depend upon the composition of the lone pair on phosphorus. In the $n = 2$ molecule, the internal CPC angle is very small and will tend to bend inward the carbon and phosphorus orbitals in order to reduce the bonding angle from its normal, unstrained value. This will cause the angle between the other hybrids on phosphorus to increase; that is, the angle between the phosphorus hydrogen, phosphorus, and the phosphorus lone pair (HPlp) will tend to become larger than normal because of the pinching-in effect of the CPC angle. This will lead to a decreased p character in the lone pair orbital, and indeed, from our analysis of the STO-3G results, one can approximate the character of the lone pair orbital in this case as $sp^{1.25}$, approaching that of a pure sp hybrid. On the other hand, in the $n = 3$ case where the ring CPC angle is much larger, the HPlp angle is approximately 116°, and the phosphorus lone pair is characterized as $sp^{2.12}$, essentially an sp^2 hybrid. Accordingly, in the $n = 2$ case, the coupling is relatively ineffective because of the lower p character of the lone pair orbital, while in the $n = 3$ molecule with an sp^2 hybrid, the coupling is much more effective, leading to a deshielding effect. The hybridization in the $n = 3$ and $n = 4$ cases is very similar to the $n = 2$ case (essentially sp^2), so it is apparently the slightly larger HOMO–LUMO gap that causes the small upfield shift in these molecules.

SUMMARY

The detailed understanding of absolute chemical shifts is a difficult task. It is usually easier, both experimentally and theoretically, to compare differences between molecules. Typically, many orbitals contribute, but often major players may be found that tend to explain trends within groups of molecules, and their contributions traced back to correct qualitative ideas that theory quantifies. We believe this to be true in the present case of the saturated monocyclic phosphines. Presently, it would be a difficult task indeed to detail the small differences between the shieldings of the larger rings ($n = 4$ and 5). On the other hand, the unusual behavior of the $n = 2$ and 3 molecules can be understood in terms of the differences in the HOMO–LUMO gaps and p character of the phosphorus lone pair . The HOMO–LUMO gap is larger than the $n = 4,5$ molecules for phosphirane ($n = 2$) but smaller in phosphetane ($n = 3$). The hybrid character of the lone pair in phosphirane ($n = 2$) is almost sp while that for phosphetane ($n = 3$) is essentially sp^2. Together, these two effects give rise to the relative shielding found for the $n = 2$ molecule and (small) relative deshielding of the $n = 3$ molecule relative to the "normal" $n = 4$ and $n = 5$ cases.

ACKNOWLEDGMENTS

We take this opportunity to express our gratitude to Bill McEwen for his outstanding leadership in promoting the field of Main Group Chemistry. His emergence in this role was a natural consequence of his long and highly accomplished career as research chemist, educator, and administrator .

We are indebted to the North Carolina Supercomputing Center for providing CPU time on the Cray T-916 platform that allowed these calculations to be carried out.

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