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An Ab Initio Study of Angle Effects on ^{31}P Nuclear Shielding in Simple Phosphines

D. B. Chesnut[1] and L. D. Quin[2]

[1]P. M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27708

[2]Department of Chemistry, University of North Carolina at Wilmington, Wilmington, North Carolina 28403

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ABSTRACT: *Ab initio shieldings for a number of methyl and ethyl phosphines agree well with experimental values. An increase of the intersubstituent angles generally causes a deshielding effect that may be understood in terms of a decrease of the HOMO-LUMO energy gap. However, α-, β-, and γ-substituent effects play a dominant role in determining the overall NMR shieldings observed. Simple additive effects involving successive replacement of hydrogen by methyl and ethyl groups are not present, and the effect on the shielding by angle changes is not sufficient to remove this nonadditivity.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 566–572, 1999

INTRODUCTION

The interpretation of the ^{31}P NMR shifts of organophosphorus compounds has presented a challenging problem from the earliest experimental observations, and although our work has shown progress in this area [1–7], many observations remain without a firm basis in theory. In these cases, empirical relationships can sometimes be developed that guide the experimentalist. However, when there is no understanding of the real cause of chemical-shift effects, interpretations based only on empiricism can give unsatisfactory conclusions. The family of phosphines well illustrates this problem. It was observed early in the collection of data for trialkylphosphines that in many cases the ^{31}P shift can be related to the magnitude of the CPC bond angle, with deshielding accompanying increases in the angle. Thus, the value is δ-62 for $(CH_3)_3P$ and δ-21 for $(CH_3CH_2)_3P$, and it is $\delta+19$ for $[(CH_1)_2CH]_3P$ and $\delta+62$ for $[(CH_3)_3C]_3P$. (Unless otherwise noted, all ^{31}P NMR shifts were taken from the compilation of Tebby [8].) Clearly the bond angles expand in this series and in some others, and this formed the basis for the empirical relation that increased bond angles in phosphines, causing flattening of the phosphorus pyramid and a change in hybridization, which causes deshielding.

The recent literature [8] confirms that the bond-angle relation is still being invoked to explain ^{31}P shift effects in phosphines. However, important exceptions are known [9,10] that suggest the bond-angle relation, although possibly real, may be subjugated by strong influences from other effects, lessening the value of the empirical relation, and even suggesting that the relation is fiction. That bond angles alone do not control the chemical shift is clearly seen by simply adding one other phosphine, $(CH_3CH_2CH_2)_3P$, to the above series; this phosphine must be, if anything, more crowded than the ethyl derivative, and thus may have increased bond angles. The ^{31}P shift, however, moves in exactly the opposite way: upfield to δ-33. Similarly, tri-isobutylphosphine, $[(CH_3)_2CHCH_2]_3P$, might be expected to have increased bond angles, but the shift moves even further upfield (δ-45) again. These chain lengthening

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Correspondence to: D. B. Chesnut

Dedicated to Professor Alfred Schmidpeter on the occasion of his 70th birthday.

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and branching effects resemble those in ^{13}C NMR and can be empirically calculated by a set of substituent factors for the β and γ carbons [9]. Exceptions to the bond-angle argument are especially abundant among cyclic phosphines, and if one worked only with this tool to explain shifts, only confusion would result. This is quite clear in the simple series $(CH_2)_nP$, values for the $n = 2$, 3, 4, and 5 compounds being δ-236, +13.9, −15.3, and −34.3, respectively, and thus are not only related to bond angles. We have addressed this problem in an earlier study [5] and developed an explanation based on the p-character of the phosphorus lone-pair orbital and on the magnitude of the HOMO-LUMO energy gap, to which we will refer later in this paper.

To our knowledge, there have been no recent applications of theory to evaluate the influence, if any, of bond angle modifications on ^{31}P NMR shifts of phosphines. Dransfeld and Schleyer [11] recently performed a principal component analysis of phosphorus substituent effects, including the substituent angle as one of the factors. They found a lack of a significant relationship between the sum of the substituent angles and the overall shielding, but did not specifically study angle modification effects. In this article, we report the results of some calculations on simple model compounds that confirm the reality of deshielding that accompanies increased bond angles. At the same time, we show that other effects, the so-called α, β, and γ effects (not specifically addressed here), must also be operating on the ^{31}P nucleus as chain lengthening and branching occur.

THEORETICAL METHODS

The structures employed in the present study were all optimized at the MP2 (frozen core) level of theory with the 6-31+G(d,p) basis set [12], and the NMR shielding calculations were performed at the MP2/6-311G(d,p) level [12] using Ditchfield's gauge including the atomic orbital (GIAO) approach [13] as implemented in the Gaussian 98 program [14]. Although the structure optimizations employed only a single set of d polarization functions for heavy atoms (and a single set of p functions for hydrogen), the chemical shielding calculations included two sets of d functions for phosphorus with the MacLean and Chandler basis set (621111,52111,11) = [$6s$,$5p$,$2d$] for the phosphorus anion [15]. All the calculations were performed on Cray T-90 and J-90 platforms located in the North Carolina Supercomputing Center.

Both MP2 and Hartree-Fock shieldings were obtained in those cases where CPU time constraints allowed. In these cases, the hybrid EMPI shielding [16], given by

$$\sigma_{\mathrm{EMP1}} = \sigma_{\mathrm{HF}} + \frac{2}{3}(\sigma_{\mathrm{MP2}} - \sigma_{\mathrm{HF}}) \qquad (1)$$

was also determined. The EMPI method yields NMR shieldings that are as accurate as many other higher order calculations and in good agreement with the experiments. Only the Hartree-Fock and EMPI shieldings are reported in our tables, but the MP2 shieldings may be derived from these results.

Except as noted, chemical shieldings calculated here are reported as absolute values. Although 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), which are 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 [8] have been converted to absolute shieldings with the absolute shielding for phosphoric acid that has been determined to be 333.8 ppm [17]. The advantage of reporting 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.

RESULTS AND DISCUSSION

The RPR' intersubstituent angles are a function of the size and bulkiness of the substituents involved. Table 1 shows these optimized angles in the methyl and ethyl (and one propyl) phosphines. Although the

TABLE 1 Optimized RPR' Angles (in degrees) in the Methyl (Me) and Ethyl (Et) Phosphines and Propylphosphine (H_2PPr), and the Mean Angle, $\bar{\varphi}$

	H–H	*H–CH$_n$*	CH_n–CH_n	$\bar{\varphi} \equiv \frac{1}{3}\sum\varphi_{ij}$
H_3P	94.71			94.71
H_2PMe	94.85	97.76		96.79
$HP(Me)_2$		97.41	99.58	98.13
$P(Me)_3$			98.65	98.65
H_2PEt	94.44	97.00		96.15
$HP(Et)_2$		96.76	100.42	97.98
$P(Et)_3$			99.39	99.39
H_2PPr	94.42	96.97		96.12
Mean error	94.61	97.18	99.51	
Standard deviation	0.18	0.36	0.63	

mean intersubstituent angle exhibits only a small variation among the molecules studied, there is a consistency among the angles involving similar substituents as expected.

Table 2 shows the Hartree-Fock and EMPI calculated and observed NMR isotropic shieldings. The second-order contribution to the shielding via MP2 was performed for those molecules whose size permitted, and in those cases the EMPI shieldings are reported as well as those for the restricted Hartree-Fock (RHF) approach. There is relatively little contribution from correlation in this particular set of molecules. Although the differences between the EMPI and RHF shieldings can be as large as twenty ppm, this is still in the noise level of shielding calculations for phosphorus [3,4]. The average error, standard deviation, and the root-mean-square error (rmse) are likewise typical for our current ability to calculate phosphorus NMR shieldings. Figure 1 shows a graph of the calculated Hartree-Fock shieldings compared with experiment values, and one can see that, aside from a positive displacement from observed values, the calculated shieldings provide a good representation of experimental results.

The central study here was to observe the behavior of the shieldings in the simple phosphines as the intersubstituent angles were modified. Input angles were typically defined with respect to a true or approximate three-fold axis in each molecule from which, of course, the intersubstituent angles themselves are readily determined. It was this angle that was varied in the study by ± 5 degrees from the equilibrium structure. Shieldings determined at the Hartree-Fock level were fit to a quadratic equation of the type shown in Table 3 where the variable is the change in the mean intersubstituent angle from its equilibrium value; the regression fit coefficients are shown in Table 3. Figure 2 illustrates the general trend of shielding where an average behavior (of the molecules studied) has been used. The shielding is slightly quadratic in the change in intersubstituent angle and decreases (in all cases) as the intersubstituent angle increases, that is, as the molecule moves towards a more nearly planar configuration around phosphorus. There is a small variation of the regression parameters in Table 3 from one structure to another, but they are all basically quite similar, which is not an unexpected result.

TABLE 2 Calculated (RHF and EMPI) and Observed Isotropic Shieldings (ppm) The mean error ($\bar{x}$), standard deviation (σ), and the root-mean-square error (rmse) are also given.

		Calculated		*Calculated − Observed*	
	Observed	*RHF*	*EMPI*	*RHF*	*EMPI*
H_3P	573	584.0	601.0	11.0	28.0
H_2PMe	497.3	508.1	520.0	10.8	22.7
$HP(Me)_2$	433.3	450.7	455.1	17.4	21.8
$P(Me)_3$	396	420.5	–	24.5	–
H_2PEt	462	470.7	479.0	8.7	17.0
$HP(Et)_2$	389.3	413.9	–	24.6	–
$P(Et)_3$	355	384.0	–	29.0	–
H_2PPr	–	478.3	–	–	–
Mean error				18.0	22.4
Standard deviation				7.5	3.9
rmse[a]				19.5	22.7

[a] root-mean-square error

Chemical shielding is caused by magnetic fields induced in a molecule by the application of an external magnetic field. As one turns on the external magnetic field, the ground state charge clouds are set in rotation giving rise to internal fields in opposition to the external field. The external field also effects a mixing of excited states, into the ground state, which partially relieves the usual quenching of orbital angular momentum and provides additional currents leading to internal field contributions that add to the external field. While the ground state charge cloud rotation is responsible for the generally large and dominant diamagnetic contribution to shielding, it is the mixing in or orbitals not represented in the ground state of the system by the application of the field, the so called paramagnetic contribution, that dominates NMR shielding differences for a given nucleus in different molecular environments. This paramagnetic contribution comes about from the scalar coupling of the angular momentum of the electron and the external field ($\mathbf{H}\cdot\mathbf{L}_j$) between orbitals. The $\mathbf{H}\cdot\mathbf{L}_j$ operators act as rotation operators that give rise to net currents about the nucleus in question. Because the theoretical approach involves perturbation theory, the coupling between orbitals is generally a function of the difference in their orbital energies. Small energy differences lead to large paramagnetic (negative) contributions to the shielding. Orbitals that lie near the Hartree-Fock HOMO-LUMO energy gap will be particularly important in this regard. For example, our understanding of why multiply bonded systems generally exhibit large paramagnetic effects is based on the picture of local π and π^* orbitals that lie closer to this energy gap than do their σ and σ^* counterparts; the energy gap between the π and π^* orbitals is smaller than those of the σ and σ^* orbitals.

Our understanding of the observed trend in shielding with angle increase is understood here in terms of the change in the HOMO-LUMO energy

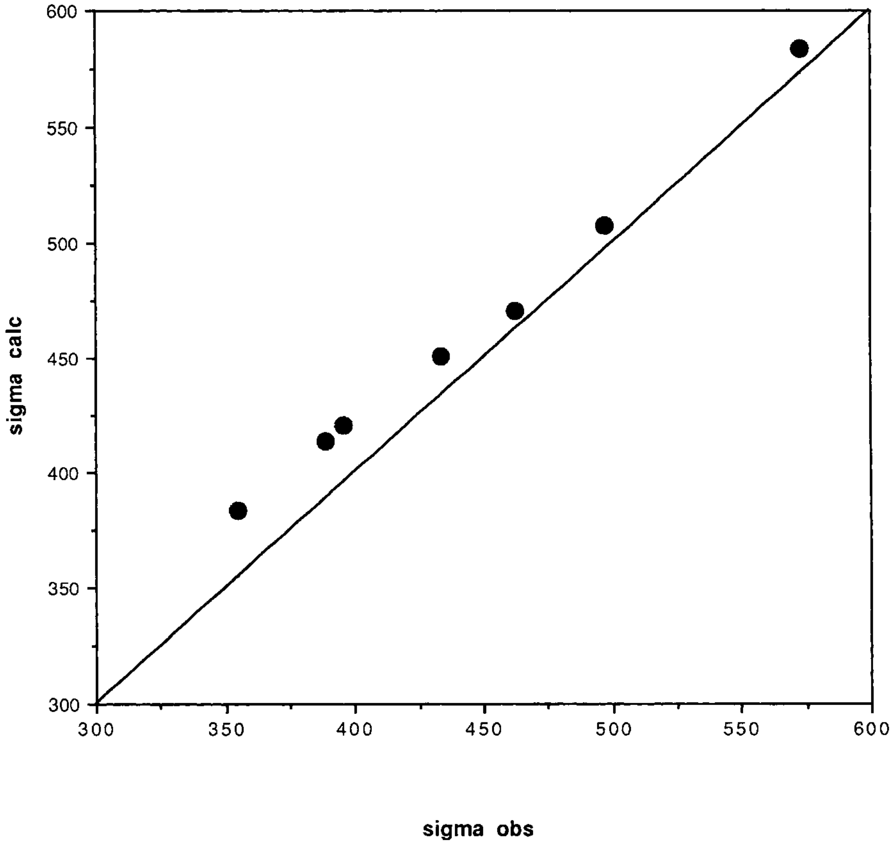

FIGURE 1 RHF calculated vs. observed absolute shieldings (sigma, ppm) for the simple phosphines in Table 2.

TABLE 3 Coefficients in the Quadratic Fit of the Shielding to Changes in the Mean Intersubstitutent Angle, $\delta\bar{\varphi} = \delta$ (1/3 $\Sigma\ \varphi_{ij}$), for the Simple Phosphines[a]

Molecule	σ_1	σ_2
PH_3	−5.57	0.154
H_2PMe	−4.09	0.180
$HP(Me)_2$	−3.92	0.218
$P(Me)_3$	−4.50	0.262
H_2PEt	−3.10	0.155
$HP(Et)_2$	−4.14	0.192
$P(Et)_3$	−5.09	0.229
H_2PPr	−3.37	0.156
Average	−4.22	0.193
Standard deviation	0.77	0.037

[a]The fit equation is: $\sigma = \sigma_0 + \sigma_1\delta\bar{\varphi} + \sigma_2\,(\delta\bar{\varphi})^2$.

gap. Generally speaking, NMR chemical shieldings are complicated and involve contributions from many orbitals. However, it may well be expected that changes in the HOMO-LUMO gap may well be reflective of either upfield or downfield shifts depending on the sign of the change of the energy gap. In the present study as the intersubstituent angles are increased, there is in all cases a concomitant decrease in the HOMO-LUMO gaps. This decrease in the energy gap will tend to effect a reduction in the difference in energy between the ground state orbitals and those virtual orbitals to which they are coupled, giving rise to the downfield or paramagnetic change in the shielding.

While the correspondence of the deshielding with angle increase and the decreased HOMO-LUMO gap around the equilibrium geometry is consistent for all the methyl and ethyl phosphine derivatives studied here, it apparently does not extend over a larger angle range. This is shown in Figure 3, where the parallel and perpendicular components of the phosphorus shielding in the PH_3 molecule are shown over a range of angles. In the vicinity of the equilibrium intersubstituent angle (94.7°), an increase of angle leads to a decrease of the isotropic shielding, but this effect is not obtained over the higher angle range. The parallel shielding component decreases in an almost linear way, but the perpendicular component is basically quadratic. The quadratic behavior of the perpendicular component dominates at higher angles, so at the planar configuration (120.0°) the calculated shielding is actually higher than in the equilibrium form; this behavior

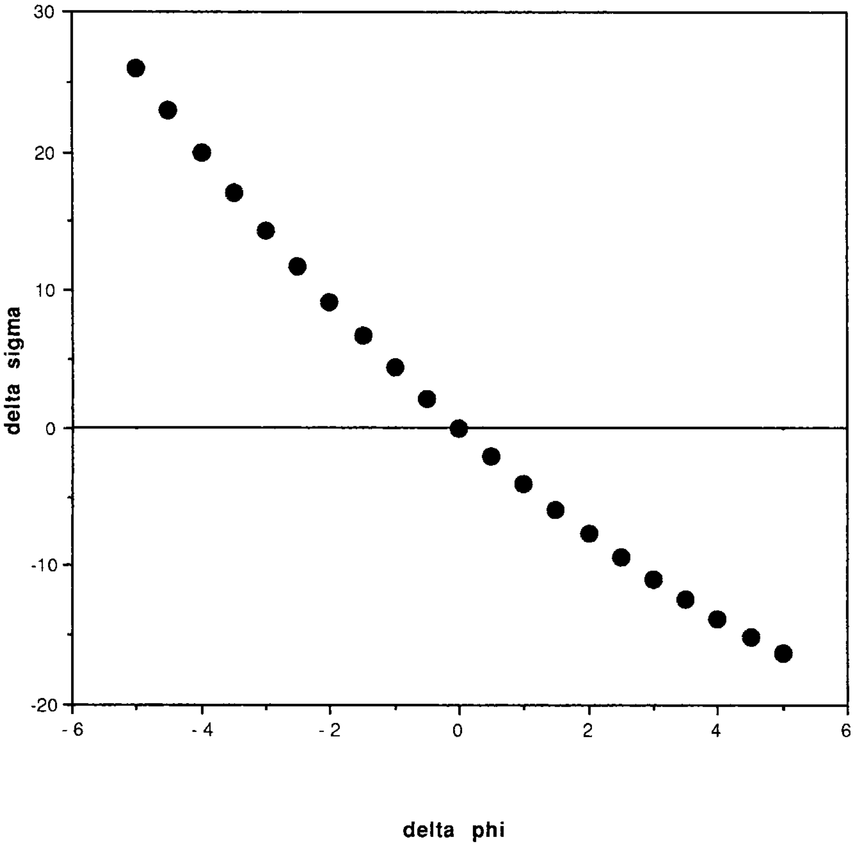

FIGURE 2 General behavior of the change in NMR shieldings (delta sigma, ppm) as a function of the change in intersubstituent angle (delta phi, degrees).

of the shielding in PH_3 was observed previously [17a,18]. This behavior is not present solely in phosphine; similar results are found in the calculated shieldings in trimethyl and triethyl phosphine. Without a detailed breakdown of the shielding contributions (unavailable in Gaussian 98), we are unable to comment further at this time on the difference in the behavior of the parallel and perpendicular components of the shielding.

The minima in the Hartree-Fock shieldings for PH_3, $P(CH_3)_3$, and $P(C_2H_5)_3$ are estimated to be 106.5, 105.5, and 109.2 degrees, respectively. The fact that the shielding minima appear at angles higher than the equilibrium angle accounts for the observed positive curvature of the general angle deshielding effect shown in Figure 3. The fact that shieldings in these molecules can actually increase with increasing the intersubstituent angle at higher angles suggests that compounds with very bulky groups surrounding phosphorus might actually show upfield shifts; however, the data presented in the Introduction for compounds like $[(CH_3)_2CH]_3P$ and $[(CH_3)_3C]_3P$ show that such is not the case for these molecules.

It may be observed that simple additive alpha and beta effects as one crosses from the primary to secondary to tertiary methyl and ethyl phosphines are not present in the cases studied here, experimentally or theoretically. That is, the addition of a second methyl group to methylphosphine does not give a change in the phosphorus shielding that is twice that of the addition of a methyl group to phosphine itself. The difference in the change of shielding is even larger for the addition of a third methyl group. Table 4 shows these effects which we label as α_1, α_2, and α_3, representing the change in shielding upon the addition of one methyl group to phosphine, of a second methyl group to methylphosphine, and of a third methyl group to dimethylphosphine; the β_1, β_2, and β_3 effects are similarly defined. Table 4 shows these effects for both the observed shieldings and the calculated shieldings in the columns marked "uncorr." (uncorrected) where no account of changes in intersubstituent angles is taken into account. Given the noise level of phosphorus NMR shielding calculations, the agreement between calculated and observed substituent effects is very good.

The fact that we have calculated the shielding in

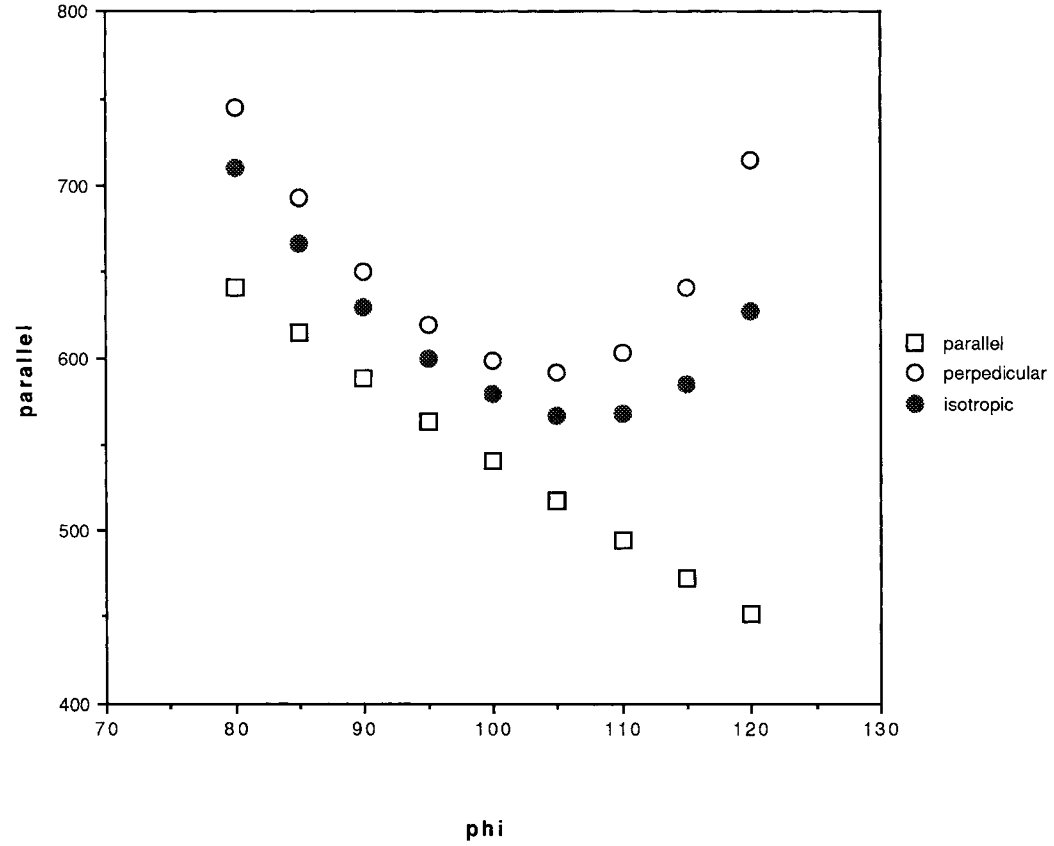

FIGURE 3 EMPI shieldings (ppm) for PH_3 as a function of the HPH angle (phi, degrees). Data are given for the shielding parallel to the principal axis (parallel), perpendicular to the principal axis (perpendicular), and the isotropic shielding (isotropic).

TABLE 4 Effect of Substituent (alpha and beta) Effects both Uncorrected and Corrected for Angle Effects[a]

	Observed Shieldings		*Calculated Shieldings*	
	Uncorr.	*Corr.*	*Uncorr.*	*Corr.*
α-1	−75.1	−63.6	−75.9	−64.4
α-2	−64.0	−58.6	−57.4	−52.0
α-3	−37.5	−34.5	−30.2	−27.2
β-1	−35.9	−37.1	−37.4	−38.6
β-2	−8.1	−7.4	0.6	1.3
β-3	2.6	8.1	0.3	5.8

[a] The uncorrected (uncorr.) observed and calculated shifts are corrected (corr.) from the calculated angular variations. All the data are in ppm.

n-propyl phosphine allows us to estimate the effect of adding a γ carbon on the phosphorus shielding. Starting with the staggered conformation of methylphosphine, the carbon chain is lengthened in the extended and staggered conformation for the ethyl and propyl molecules, maintaining a plane of symmetry. We find the shift in propylphosphine to be +7.6 ppm upfield of the value for ethylphosphine. This is consistent with experimental observations that give a value of 7–10 to the gamma substituent effect in primary phosphines [9].

One may ask whether or not the lack of uniform alpha or beta effects is because the different structures have different mean intersubstituent angles. In order to address this question, we used the regression fit equation shown in Table 3 for the change in shielding with change in angle to correct both the observed and calculated shieldings to a mean intersubstituent angle of 97.4°, which is the average mean angle for phosphine and its methyl and ethyl derivatives. These corrected substituent effects are shown in the columns marked "corr." (corrected) in Table 4, where it is seen that this correction does not remove the lack of uniformity in the substituent effects. (Corrections made in the single estimate of the gamma effect described previously change it only modestly, from +7.6 to +7.1.)

SUMMARY

Ab initio shieldings for a number of methyl and ethyl phosphines agree well with experimental values. An increase of the intersubstituent angles generally causes a deshielding effect that may be understood in terms of a decrease of the HOMO-LUMO energy gap. However, alpha, beta, and gamma substituent effects play a dominant role in determining the overall NMR shieldings observed. Simple additive effects involving successive replacement of hydrogen by methyl and ethyl groups are not present, and the effect on the shielding by angle changes is not sufficient to remove this nonadditivity.

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REFERENCES

[1] Chesnut, D. B.; Quin, L. D.; Moore, K. D. J Am Chem Soc 1993, 115, 11984.
[2] Chesnut, D. B.; Quin, L. D. J Am Chem Soc 1994, 116, 9638.
[3] Chesnut, D. B.; Rusiloski, B. E. In Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis; Quin, L. D., and Verkade, J. G., Eds.; VCH Publishers: New York, 1994; Chapter 1.
[4] Chesnut, D. B.; Byrd, E. F. C. Heteroatom Chem 1996, 7, 307.
[5] Chesnut, D. B.; Quin, L. D.; Wild, S. B. Heteroatom Chem 1997, 8, 451.
[6] Chesnut, D. B. Chem Phys 1997, 224, 133.
[7] Chesnut, D. B.; Quin, L. D. In Advances in Molecular Structure Research; Hargittai, M., Hargittai, I., Eds.; JAI Press: in press; Vol. 5, 1999.
[8] Tebby, J. C. Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data; CRC Press: Boca Raton, FL, 1991.
[9] Quin, L. D.; Breen, J. J. Org Magn Reson 1973, 5, 17.
[10] Gorenstein, D. G. Phosphorus-31 NMR; Academic Press, Inc.: New York, 1984.
[11] Dransfeld, A.; Schleyer, P. v. R. Magn. Reson Chem 1998, 36, S29.
[12] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley & Sons: New York, 1986.
[13] Ditchfield, R. Mol Phys 1974, 27, 789.
[14] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; and Pople, J. A. Gaussian 98, Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.
[15] MacLean, A. D.; Chandler, G. S. J. J Chem Phys 1980, 72, 5639.
[16] Chesnut, D. B. Chem Phys Lett 1995, 246, 235.
[17] (a) Jameson, C. J.; de Dios, A. C.; Jameson, A. K. J Chem Phys 1991, 95, 9042; (b) Jameson, C. J.; de Dios, A. C.; Jameson, A. K. Chem Phys Lett 1990, 167, 575.
[18] Chesnut, D. B.; Foley, C. K. J Chem Phys 1986, 85, 2814.