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Characterization of NMR Deshielding in Phosphole and the Phospholide Ion

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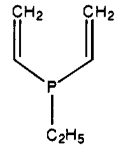
Abstract: Ab initio chemical shielding calculations employing the gauge including atomic orbtial (GIAO) method have been carried out on phosphole, the phospholide ion, and related thiophene, pyrrole, and furan compounds, to provide an understanding of the NMR shieldings observed in the phosphole systems. Structure and energy considerations in phosphole constrained to be fully planar (as opposed to being nonplanar and pyramidal) show that the system is conjugated but that this conjugation is in itself not responsible for the observed deshielding effect. Rather, it is shown that removing the stabilizing proton from the PH bond in phosphole to form the phospholide ion allows the system to become essentially fully conjugated and creates a lone pair only weakly coupled to the ring, and that this in-plane lone pair is responsible for the large downfield (paramagnetic) shifts seen in the ion relative to the parent compound.

Introduction

The first example of a phosphole, the fully unsaturated five-membered ring containing phosphorus, was announced in 1959,[1,2] but it was not until 1967 that the ^{31}P NMR spectrum was recorded for a phosphole.[3] This compound, 1-methylphosphole, was prepared for the purpose of intiating studies on the possibility that the phosphole ring system possessed a degree of cyclic electron delocalization, or aromaticity, so characteristic of the other members of the heterocyclopentadiene family, thiophene, pyrrole, and furan. The ^{31}P NMR shift for 1-methylphosphole was 337.1 ppm[4] (δ -8.7), and similar values for other *P*-methylphosphole derivatives were observed later (e.g., 3-Me, 335.3 ppm (δ -6.94); 2-Me, 335.7 ppm (δ -7.34);[5] larger substituents on phosphorus gave even further downfield shifts (e.g., 1-benzyl, 320.5 ppm (δ +7.9);[6] isobutyl, 322.9 ppm (δ +5.5)[7]). Of special significance was the observation that the shifts were noticeably downfield of that for an open-chain divinylphosphine (**1**).

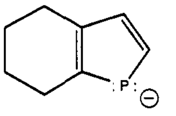


1

σ_P= 349.2 ppm (δ-20.8)

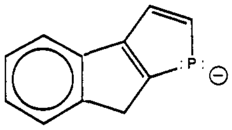
Since some other properties were suggestive of delocalization in the phosphole ring,[8] the downfield ^{31}P NMR shift was attributed to this effect. It was later reported from the same laboratory,[6,9] using X-ray analysis of the solid 1-benzylphosphole, that, unlike nitrogen in a pyrrole, the substituent on phosphorus in a phosphole was noticeably displaced from the plane of the ring, and thus phosphorus had retained the normal pyramidal character found in all phosphines. This was also deduced from stereochemical studies in solution.[10] Over the years additional information on the phosphole system was gathered, and a picture has developed[11] of a system with relatively little delocalization, retarded because of the pyramidal structure at phosphorus. This was placed on a numerical basis by the calculation of "aromaticity indices" derived from experimental bond order values[12] which resulted in the conclusion that the phosphole ring is the least delocalized of the heterocyclopentadiene family, but not greatly less so than furan.

Later it was discovered that the phospholide ion had much greater deshielding of ^{31}P, first noted in structures **2** and **3**,[13] but later confirmed in monocyclic phospholids[14] (e.g., the parent **4**).



2

σ_P= 255.1 ppm (δ+73.3)



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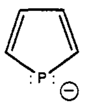
σ_P= 246.7 ppm (δ+81.7)



4

σ_P= 251.2 ppm (δ+77.2)

In the ion, the pyramidal structure at phosphorus is absent and the system is isoelectronic with thiophene. This strong deshielding was attributed to the cyclic delocalization in the ion; this would impart more double bond character to the PC bond, a well-known strong deshielding effect.[15] Others have also adopted the view that the strong deshielding in the phospholide ion is indicative of a highly delocalized system.[16]

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[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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[4] Chemical shieldings reported in this paper are given in parts per million (ppm) on an absolute basis as is the form in which they are calculated theoretically. They may readily be converted to chemical shifts relative to 85% phosphoric acid (shown in parentheses as positive or negative δ-values) by using the absolute shielding for this species which is found to be 328.4 (Jameson, C. J.; de Dios, A. C.; Jameson, A. K. *Chem. Phys. Lett.* **1990**, *167*, 575). Experimental shifts, likewise, were converted to absolute shieldings using the absolute shielding for phosphoric acid. See the discussion under Calculational Details.

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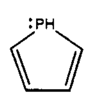
In the present paper, we inquire by *ab initio* computational methods into the origin of the deshielding in the neutral phosphole and phospholide ion structures, with special emphasis on the difference in shielding between these two. We have had success in the interpretation of the large deshielding in the 7-phosphanorbornene system[17] by these methods, and show here that such an approach provides a proper characterization of the shielding effects in the phosphole systems.

Calculational Details

Shielding calculations were carried out employing Ditchfield's gauge including atomic orbital (GIAO) coupled Hartree–Fock method.[18] The structures investigated included phosphole (**5**) and the phospholide ion (**4**), thiophene (**6**) and its protonated form (**7**), pyrrole (**8**) and the nitrogen-deprotonated pyrrole ion (**9**), and furan (**10**). The saturated (tetrahydro) forms of all the neutral unsaturated species were also studied. In the case of the phosphole and thiophenium compounds, the fully planar species as well as the equilibrium nonplanar pyramidal species were examined. Calculations were also carried out for the methyl derivatives of both the pyramidal and fully planar forms of phosphole and confirmed that the bulkier methyl compound yields the same basic effect as the simpler hydrogen compound.



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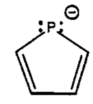

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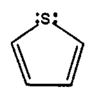

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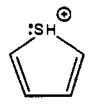

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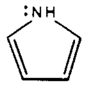

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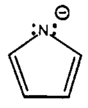

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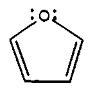

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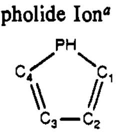
The basis sets employed were the valence triple-ζ with polarization (6-311G(d,p)) for carbon and hydrogen[19] (a [4s,3p,d/3s,p] basis with six Cartesian d functions), and the McLean–Chandler 12s, 9p basis[20] in the contraction (631111/42111) = [6s,5p] for phosphorus and sulfur with either one or two sets of (six) d polarization functions. A single set of d functions was employed for phosphorus and sulfur for the structural optimizations using the standard exponents in the Gaussian 92 code;[21] for the chemical shielding calculations two sets of d functions were used for these two nuclei where the standard exponents were multiplied and divided by a factor of 2 as suggested by Frisch et al.[22] so that the d-exponent ratios were always equal to 4. The structures employed for the shielding calculations were optimized at the level of basis indicated with appropriate symmetry constraints.

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 have been converted to absolute shieldings using the absolute shielding for phosphoric acid that has been determined to be 328.4 ppm.[4] 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.[23]

Table 1. Calculated and Observed Distances (Å) and Angles (deg) for Phosphole and the Phospholide Ion[a]



	phosphole		phospholide ion	
distance	observed[b]	calculated[c]	observed[d]	calculated
PC_1	1.786(5)	1.817	1.750(5)	1.764
PC_4	1.780(4)		1.752(4)	
C_1C_2	1.343(6)	1.332	1.396(5)	1.376
C_3C_4	1.343(7)		1.396(7)	
C_2C_3	1.438(6)	1.471	1.424(7)	1.416

	phosphole		phospholide ion	
angle	observed	calculated[c]	observed	calculated
C_4PC_1	90.7(2)	89.68	90.5(2)	89.71
PC_1C_2	109.9(3)	110.63	112.2(4)	112.23
PC_4C_3	110.1(3)		112.4(4)	
$C_1C_2C_3$	114.1(4)	114.19	112.6(4)	112.92
$C_2C_3C_4$	114.1(4)		112.2(4)	
C_1PR[e]	105.9(2)	100.68		
$C(_4C_1)PR$[e,f]	66.9[g]	73.79		

[a] The experimental data are for the 1-benzyl derivative of phosphole and the lithium salt with tetramethylethylenediamine; experimental uncertainties in the last decimal point are given in parentheses. [b] Reference 9. [c] Calculated results for nonplanar, pyramidal phosphole with phosphorus displaced from the ring carbon plane by 0.168 Å. [d] Reference 25. [e] R is the benzyl carbon for the observed structure, and R = H for the calculated structure. [f] Acute angle the PH bond makes with the C_4C_1P plane. [g] Calculated from the data in ref 9.

The molecular orbitals were analyzed using modules designed for the Convex Applications Visualization System (AVS) and a partitioning program designed to divide the shielding into atomic and molecular orbital contributions. All the calculations were carried out on a Cray Y-MP located in the North Carolina Supercomputing Center.

Results

Since some of the structural parameters are currently unknown and in order to achieve consistency of interpretation, all structures were optimized at the Hartree–Fock level. The structures of pyrrole, furan, and thiophene are known as well as the tetrahydro derivatives of the latter two molecules.[24] The crystal structure of the phosphorus-substituted benzyl derivative of phosphole has been worked out,[6,9] and recently that of the lithium salt of the phosphole ion in which the lithium coordinates both to the phosphole ring and to the nitrogens of tetramethylenediamine also contained in the structure.[25] The ring data for phosphole and the phospholide ion compared to experiment are given in Table 1, while a compilation of calculated ring distances in the unsaturated species containing both first- and second-row heteroatoms is given in Table 2. Our calculated structures agree reasonably well with experiment, showing a root mean square difference of 0.021 Å in the bond lengths and 0.52° in the bond angles, agreement typical of structures calculated at the Hartree–Fock level. The calculated PC distance in phosphole is noticeably longer than that observed for the 1-benzyl derivative, as is the formally single CC bond. Note that in both the calculated and experimental phosphole structures, the phosphorus atom is pyramidal and displaced from the carbon atom plane by a small amount; a similar situation obtains for the calculated thiophenium ion.

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(23) Employing the basis sets used here, a shielding of 332.9 ppm is calculated for PO_4^{-3}; see: Chesnut, D. B.; Rusiloski, B. E. *Chem. Phys.* **1991**, *157*, 105.

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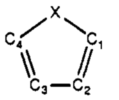
Table 2. Calculated Bond Lengths (Å) for First- and Second-Row Unsaturated Five-Membered-Ring Species[a]



A. First-Row Species

X =	X = :C⁻	X = NH	X = :N⁻	X = O
C_1C_2	1.403	1.358	1.388	1.338
C_2C_3	1.403	1.427	1.412	1.442
C_1X	1.403	1.362	1.344	1.342

B. Phosphorus Species

X =	X = PH[b]	X = PH (planar)[b]	X = :P⁻
C_1C_2	1.332 (1.332)	1.373 (1.382)	1.376
C_2C_3	1.471 (1.472)	1.420 (1.409)	1.416
C_1X	1.817 (1.816)	1.718 (1.709)	1.764

C. Sulfur Species

X =	X = SH⁺	X = SH⁺ (planar)	X = S
C_1C_2	1.323	1.335	1.345
C_2C_3	1.473	1.453	1.436
C_1X	1.780	1.739	1.725

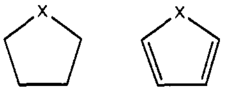
[a] Forced fully planar species are indicated as "planar" in parentheses. [b] Values for the methyl derivative, PCH_3, are given in parentheses.

As previously mentioned, we calculated structures (and shielding) for both the equilibrium nonplanar pyramidal phosphole structure and the nonequilibrium fully planar form. The fully planar species is calculated to be 25.8 kcal/mol higher in energy. In pyramidal phosphole the phosphorus is found to be 0.168 Å out of the carbon plane, in good agreement with the value of 0.208 Å found in the benzyl derivative.[9] The advantage of using as a model the planar ring molecule is that it removes one essentially unnecessary degree of freedom and makes our later shielding analysis simpler. Our results for phosphole are essentially identical to those of Hughes and Edgecombe[26] who studied this species with a very slightly smaller (6-311G(d)) basis (but who apparently constrained phosphorus to lie in the plane of the carbon atoms), and are similar to those of Baldridge and Gordon[27] who used the much smaller 3-21G(d) basis, and to those of Bachrach[28] who optimized at the 6-31G(d) level. Bachrach also reoptimized his structures at the MP2/6-31G(d) level, and reports small bond length changes; upon including correlation at the MP2 level, his PC distance changed from 1.818 to 1.800 Å, the C_1C_2 length from 1.333 to 1.362 Å, and the C_2C_3 distance from 1.470 to 1.451 Å, changes which slightly improve agreement with experiment.

There is some interest in the angles the PR (R = phosphorus substituent) bond makes in these structures. As indicated in Table 1, the C_1P–(benzyl)C angle in the benzyl derivative of phosphole is 5° larger than that calculated for the C_1PH angle in phosphole itself. Furthermore, the acute angle the PR bond makes with the C_4C_1P plane is considerable smaller in the benzyl derivative (66.9°) than in the calculated phosphole (73.79°). This is likely a result of the difference in size of the substituting groups. A similar effect is seen in methyl phosphole where, relative to the R = H parent compound, this angle is reduced to 69.80°. One might well expect this angle to tend to 0° (coplanarity) as the bulk of the substituting group is increased, such as in the three examples cited here.

The structures for the tetrahydro (saturated) species were optimized for the envelope, twist, and planar forms. The twist (half-chair, C_2) forms are typically the lowest in energy, with the exception of the anti-envelope form of tetrahydropyrrole (pyrrolidine) which was calculated to be approximately 0.7 kcal/mol below that of the twist form. The planar forms were all higher in energy by 4–7 kcal/mol. The shielding calculations of the tetrahydro species reported in Table 3 are those of the twist or half-chair forms.

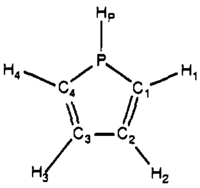
Table 3. Heteroatom Calculated Absolute Shieldings (in ppm) and Calculated and Observed Changes in Shifts (Δδ, ppm) for Saturated and Unsaturated Five-Membered Ring Species[a]



X	saturated	unsaturated	Δδ(calcd)	Δδ(obsd)
NH	246.4	120.2	126.2	107[b]
:N⁻		−27.5		
O	331.1	80.0	251.1	222[c]
SH⁺		434.2		
SH⁺ (planar)		451.7		
S	579.7	336.7	243.0	303[d]
PH	435.0	405.8	29.2	
PH (planar)		396.8		
:P⁻		294.9		
PCH_3	400.6	365.3	35.3	
PCH_3 (planar)		354.4		

[a] The saturated species are half-chair, C_2 species, while the phosphole and thiophenium species are pyramidal unless otherwise indicated as (fully) planar. [b] Reference 29. [c] Reference 30. [d] Reference 31.

Table 4. Calculated and Observed Absolute Shieldings (ppm) for Neutral Phosphole and the Phospholide Ion[a]



	phosphole		phospholide ion			
	calcd	obsd	calcd	obsd	Δδ(calcd)	Δδ(obsd)
P	405.8	377.6	294.9	251.2	110.9	126.4
C_1	58.9	53.0	56.8	54.4	2.1	−1.4
C_2	50.5	43.4	77.0	64.4	−26.5	−21.0
H_1	25.57	23.74	25.23	24.06	0.34	−0.32
H_2	25.34	23.51	26.03	24.22	−0.69	−0.71
H_p	27.31	25.65				

[a] The absolute shielding of phosphorus in phosphoric acid of 328.4,[4] carbon in TMS of 184.1,[32] and hydrogen in TMS of 30.84[33] have been used to convert the experimental shifts in ref 14b to absolute shieldings.

The NMR chemical shieldings of the saturated and unsaturated species are given in Table 3 along with calculated differences in moving from the saturated to the unsaturated species and, where available, the differences observed. Table 4 shows a detailed comparison for all nuclei of calculated and observed shieldings for phosphole and its ion where the experimental data have been taken from the work of Charrier and Mathey[14b] who studied the hydrogen, lithium, and phenyl phosphorus derivatives of a number of methyl and phenyl ring-carbon-substituted phospholes. We have converted the relative chemical shifts of Charrier and Mathey to absolute shieldings using the absolute shielding of phosphoric acid of 328.4,[4] carbon in TMS of 184.1,[32] and hydrogen in TMS of 30.84.[33] The agreement between calculated and observed shieldings for all the species shown in the table is typical of the relatively good agreement between theory and experiment one can obtain with the Hartree–Fock/GIAO approach using an extended basis set; generally speaking, with the exception of hydrogen, one can calculate such shieldings to 3–4% of the

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shielding range of a nucleus.[34] Hydrogen is a difficult species to determine theoretically on an absolute basis (relative shieldings are calculated better); as shown in Table 4, the hydrogen shieldings are typically calculated to be too high (too diamagnetic) by anywhere from 1 to 2 ppm. It is clear from Table 4, however, that the shielding changes in moving from phosphole to the phospholide ion are well reproduced by theory, and that analyses of the wave functions resulting from our calculations can be expected to reveal the proper physical cause of the large deshielding observed.

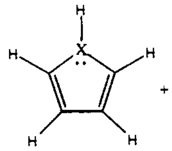
Discussion

The essential result of our calculations is that the large deshielding seen in the phospholide ion is not due directly to the conjugated nature of that species, but rather is an indirect consequence of the conjugated nature of the phospholide ion in that the in-plane lone pair in the ion has an orbital energy significantly closer to the HOMO–LUMO gap than the lone pair in phosphole. It is desirable, however, before presenting an analysis of the shielding results, to discuss the conjugated nature of phosphole in its several forms. We do not intend to delve deeply into the question of "aromaticity" (cyclic conjugation) in this system, but rather to point out that while pyramidal phosphole appears to be only weakly conjugated from the structural and energy standpoints, the data suggest that both planar phosphole and the phospholide ion are strongly conjugated, although significant deshielding is found only in the ion.

A. Structural Considerations. Table 2 shows the calculated bond lengths for the neutral and charged forms of phosphole and thiophene as well as some first-row analogs. While the lowest energy form of phosphole (PH) and the thiophenium ion (SH$^+$) are theoretically determined to be pyramidal and nonplanar, the first-row analogs are planar. An examination of the C_1X distance as one moves through the series consisting of the cyclopentadienide ion, pyrrole, the pyrrole ion, and finally furan shows that this distance is very close to the average of the appropriate single and double bond lengths between the carbon and X-atom involved. the C_2C_3 formal single bond shows significant shortenings in all cases, while the C_1C_2 formal double bond shows (with the exception of furan) significant lenghtening. These results typify our understanding of these systems as relatively highly conjugated planar molecules.

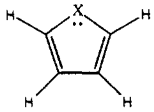
The case for phosphole is different. The formal single and double bond lengths are close to ordinary single and double bond lengths, while the C_1P distance is essentially that for a CP single bond.[35] This changes dramatically when both phosphorus and its proton in phosphole are forced into a planar configuration (PH (planar)) or when the phosphorus proton is removed, leading to the phospholide ion. In these two cases there is significant shortening of the C_1P and C_2C_3 bonds, and a commensurate lengthening of the C_1C_2 bond. On the basis of these results, we would conclude, as have others, that the phospholide ion is conjugated (as is planar phosphole) while phosphole itself is not. In the case of thiophene and its protonated form, somewhat similar results obtain. The C_1S distance shows significant lengthening when the stable, pyramidal thiophenium ion is created; the formal single and double carbon–carbon bonds in that species are also more closely related to pure single and double bonds than those in the forced-planar thiophenium ion and in thiophene itself, although the changes are not as large as those seen in the corresponding phosphorus cases.

B. Energy Considerations. There are a variety of ways to determine ring stabilization (resonance) energies. Conventional methods[36] involve heats of hydrogenation or combustion and average bond energies, while a more recent approach is to consider the energy changes upon isodesmic bond separation reactions.[37] Because conventional heat data are not available for many of the species we consider here, we have chosen the isodesmic bond separation method as a way to view the relative cyclic conjugation energies. In this approach, the energy change, ΔE, for reactions such as



$$+ XH_3 + 4CH_4 = 2CH_2CH_2 + CH_3CH_3 + 2XH_2CH_3 \quad (1)$$

for the X = P, S$^+$, and N species or



$$+ XH_2 + 4CH_4 = 2CH_2CH_2 + CH_3CH_3 + 2XHCH_3 \quad (2)$$

for the X = P$^-$, S, O, and N$^-$ species is calculated employing optimized structures. Isodesmic reactions are those in which the numbers of each formal bond type are conserved and only the relationships among the bonds are changed; bond separation reactions are those in which all formal bonds between heavy (non-hydrogen) atoms are separated into the simplest parent (two-heavy-atom) molecules containing the same kinds of linkages. The energy involved is not an enthalpy change, and no corrections for zero-point energies are made. Note for the pyrrole, phospholide, and thiophenium ions that :N$^-$, :P$^-$, and SH$^+$ ionic species are involved with some of the simpler molecules in the reactions.

Using a smaller 3-21G(d) basis, Baldridge and Gordon[27] have tabulated energy differences for isodesmic reactions involving both five- and six-membered rings, as well as energy differences for the homodesmic reactions of George, Trachtman, and Brett[38] in which formal states of hybridization as well as bond type are preserved, and the hyperhomodesmic reactions of Hess and Schaad[39] which conserve formal bond types, states of hybridization, and also specific bond fragments. We show our results for the bond separation isodesmic reactions in Table 5 along with those tabulated by Baldridge and Godon, and semiempirical resonance energies presented by Wheland[36] based on a heat of combustion approach of Klages.[40]

Our isodesmic bond separation calculations indicate that phosphole has a significantly smaller cyclic conjugation energy (13.18 kcal/mol) than thiophene (26.99 kcal/mol) but that the phospholide ion has significantly more (51.35 kcal/mol). Pyrrole is more stable in this regard than furan (38.14 vs 32.29 kcal/mol), and as might be expected in analogy with the phospholide ion, the pyrrole ion has a much greater delocalization energy (84.82 kcal/mol). In agreement with the structural considerations, one is led by the energy data to conclude that phosphole is only weakly conjugated but that the phospholide ion is strongly conjugated and delocalized. It is significant to also note that the change from planar thiophene to the nonplanar, pyramidal thiophenium ion indicates almost a complete removal of the ring stabilization energy present in thiophene.

It should be pointed out that the resonance energy ordering of the various molecules as determined by the isodesmic bond separation approach is different than that given by the semiempirical approach, and that, with the exception of thiophene, the magnitudes of the energies differ by about a factor of 2. The two

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Table 5. A Comparison of Cyclic Conjugation Energies (kcal/mol) from Isodesmic Bond Separation Reactions at the 6-311G(d,p) Level of the Present Work and the 3-21G(d) Calculations Tabulated by Baldridge and Gordon[27] and Empirical Resonance Energies Tabulated by Wheland[36]

X	6-311G(d,p)	3-21G(d)	empirical
	A. Six-Membered Rings		
CH	55.80	60.18	36.0
N	58.36	64.19	27.9
SiH	40.88	46.44	
P	50.15	56.56	
	B. Five-Membered Rings		
:CH$^-$	81.89		
NH	38.14	42.70	21.2
:N$^-$	84.82		
O	32.29	32.37	15.8
PH	13.18	12.23	
:P$^-$	51.35		
S	26.99	30.21	28.7
SH$^+$	3.58		

approaches involve different chemical reactions and, therefore, different measures (definitions) of resonance energies, and their numerical values are not expected to be the same. We are not concerned with these differences here, but rather emphasize through the isodesmic bond separation approach the relative comparison of phosphole with the phospholide ion and that of thiophene with the thiophenium ion and these relative comparisons with the calculated (and observed) shielding changes.

Our energy data are in general agreement with those of Baldridge and Gordon[27] although the phosphole structure they report has a CPC angle 10° smaller (81.6°) than ours (and experiment). Baldridge and Gordon go on to comment that their calculations for the phosphole hyperhomodesmic reaction exhibit a small negative energy difference, which they interpret as meaning that the delocalization energy arises principally from the butadiene portion of the ring. Hyperhomodesmic reactions are much more complicated than isodesmic reactions, and purportedly measure the effect of "cyclizing" an already delocalized structure. For the isodesmic reaction involving *cis*-butadiene, we calculate an energy difference at the 6-311G(d,p) level of only 6.62 kcal/mol (and only 10.70 kcal/mol for *trans*-butadiene). This is consistent with the general understanding that the butadienes are relatively nondelocalized, and does indeed suggest that our calculated phosphole isodesmic energy difference of 13.18 kcal/mol represents only a weak stabilization energy due to the five-membered-ring structure as measured by our energy calculations and those of Baldridge and Gordon.

C. Shielding Considerations. The calculated absolute shieldings (ppm) for saturated and unsaturated five-membered-ring species are given in Table 3. For pyrrole, furan, and thiophene there is a significant change in the chemical shift upon moving from the tetrahydro to the fully unsaturated forms whereas such is not the case for phosphole (or 1-methylphosphole). Phosphole and its methyl derivative show relatively small paramagnetic shift changes on the order of 30 ppm, whereas the phospholide ion is shifted downfield by over 100 ppm with respect to both phosphole and its forced planar species. It is important to note that while we have concluded that phosphole and its forced planar counterpart are conjugated to different degrees, both show essentially the same shielding results for both the hydrogen and methyl derivatives. It is only in the ion that large deshielding occurs. We conclude, then, that it is not conjugation per se which leads to the large deshielding in the ion but rather another factor.

The behavior of thiophene and the thiophenium ion confirms this analysis. While thiophene itself shows a large deshielding relative to its saturated species, as soon as it is protonated either in the equilibrium nonplanar, pyramidal form or in the nonequilibrium fully planar form, a large upfield shift occurs.

D. Cause of Deshielding in the Phospholide Ion. 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. In the case of Ditchfield's GIAO approach,[18] this division may be made by defining as "diamagnetic" those contributions which are linear in the zeroth-order (unperturbed) density matrix, and by terming those contributions "paramagnetic" which are linear in the first-order perturbed density matrix. It has been known for some time that the paramagnetic terms generally dominate changes in shielding for a particular (non-hydrogen) nucleus as its molecular environment is modified. This is also true for the phosphole species calculated here where the range of diamagnetic effects is only 9.4 ppm compared to the overall range of shieldings of 140.1 ppm.

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 which 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.

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 which 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 30 years ago.[41]

Application of these basic ideas to the present molecules is seen when one breaks down the various contributions to the shielding in terms of the molecular orbitals involved. The main contributors to the shielding-determining paramagnetic term are those coupling between orbitals occupied in the Hartree–Fock ground state and those empty (the virtual orbitals). As might be expected, in (pyramidal) phosphole and its planar forms those molecular orbitals near the HOMO–LUMO gap having sizable amplitudes in the region of the PH bond and the lone pair are major players in the paramagnetic shielding, but they do not yield contributions to the shielding that are sufficient to cause it to move significantly downfield of the tetrahydro derivative. It is only in the phospholide ion that significant deshielding is seen.

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An analysis of planar phosphole and the phospholide ion is convenient since their symmetries are identical and their principal shielding axes coincide. We are permitted to compare the optimized ion with the nonequilibrium planar phosphole since the latter is for all practical purposes indistinguishable in terms of its chemical shielding from the equilibrium nonplanar, pyramidal form of phosphole. It is found that the largest change (a large deshielding change) in the two species occurs when the magnetic field lies in the plane of the phosphate ring but at right angles to the C_2 symmetry axis, and involves a ground-state orbital of A_1 symmetry coupling with an excited π^* orbital and also to a phosphorus-p-dominated orbital in the virtual space, both of B_1 symmetry. The ground-state orbital in the case of planar phosphole has a large contribution in the PH bonding region while phosphorus p orbitals contribute to the virtual states significantly. The major change in moving from planar to ionic species is the energy shift of the contributing A_1 ground-state molecular orbital (which, by the way, is not the HOMO orbital). All the orbitals lying near the HOMO–LUMO gap in the ion show a general energy shift upward as one might expect for a negatively charged species where, because of removal of the hydrogen, the electron–electron repulsions are less compensated for than in the neutral species. The contributing A_1 orbital in the ion, however, is shifted considerably higher in energy than the others by approximately 112 kcal/mol. That is, while the contributing molecular orbitals are of the same general composition in the two species and while the excited-state orbitals tend to move up in energy about the same amount, the contributing ground-state molecular orbital moves up much more in the ion, reducing the energy difference between it and the virtual orbitals with which it interacts; this leads to a significant increase in the negative, paramagnetic contribution to the shielding and is the reason for the large deshielding seen as one moves from the planar (or neutral) form of phosphole to the ion. Physically, what is happening in this important occupied molecular orbital is simply that the significant PH bonding contribution in the neutral species now is changed over to one described by the newly created lone pair; the creation of the in-plane lone pair on phosphorus and its movement to higher energy has come about by removing the stabilizing proton from the PH single bond.

These results suggest that a similar, extra deshielding should occur in pyrrole upon deprotonation of nitrogen, and as shown in Table 3, this is indeed the case. Whereas pyrrole is 126.2 ppm more deshielded than tetrahydropyrrole, the pyrrole ion is further deshielded by a very large 147.7 ppm. The molecular orbital analysis for pyrrole and its ion reveals exactly the same cause as in planar phosphole and the phospholide ion; the creation of the lone pair that only weakly interacts with the ring system significantly raises the energy of a strongly contributing occupied molecular orbital, leading to a large paramagnetic effect.

Finally, since the phospholide ion and thiophene are isoelectronic, one might well expect the reverse effect of upfield shifts upon protonation of thiophene. This is confirmed by the data in Table 3 which show that both the pyramidal and forced fully planar thiophenium ions are shifted upfield of thiophene itself by approximately 100 ppm.

E. Summary. Ab initio chemical shielding calculations employing the gauge including atomic orbital (GIAO) method have been carried out on phosphole, the phospholide ion, and related sulfur, oxygen, and nitrogen analogs to provide an understanding of the shieldings observed in the phosphole systems. Structure and energy considerations in phosphole where the PH subsystem is constrained to reside in the plane of the heavy atoms (as opposed to equilibrium nonplanar pyramidal phosphole) show that the system is conjugated but that this conjugation in itself is insufficient to cause the observed deshielding effect. Rather, it has been shown that removing the stabilizing proton from the PH bond in phosphole allows the system to become more fully conjugated and creates a lone pair only weakly coupled to the ring and that this in-plane lone pair is responsible for the large downfield, paramagnetic shift seen in the ion relative to the parent compound.

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