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ON THE AROMATICITY OF PHOSPHOLES AS STUDIED BY ^{13}C NMR OF 1-PHENYLPHOSPHOLE

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Interest in phosphole chemistry during the last decade has mainly concentrated on two aspects: (i) the preparation of less heavily substituted derivatives with the purpose of (ii) assessing the degree of electron delocalization ("aromaticity") in this five-membered heterocyclic system by various experimental techniques (X-ray [1,2], ^{1}H and ^{31}P NMR [1,3-6], UV [3,4], etc.) and semiempirical calculations [7].

In order to contribute to the elucidation of the degree of aromaticity in phospholes, we have undertaken an investigation of their ^{13}C NMR spectral parameters. In this note we wish to report on the first determination of ^{13}C chemical shifts and signs and magnitudes of ^{13}C-^{31}P spin coupling constants in a phosphole: 1-phenylphosphole (I). Furthermore, the corresponding parameters in 1-phenyl-2-phospholene (II) and divinylphenylphosphine (III) have been determined for purposes of comparison. In view of the inaccessibility of unsubstituted phosphole, 1-phenylphosphole [3] was investigated for the following reasons: (i) no ring-carbon substituent effects have to be taken into account for the phosphole ring ^{13}C NMR data; (ii) as recently suggested from ^{31}P and ^{1}H chemical shift data [6], and as judged from X-ray analyses [1,2], a higher degree of electron delocalization is expected in (I) than for a polysubstituted derivative; (iii) our current interest in ^{13}C NMR parameters of arylphosphines [8a-d] makes a phosphorus phenyl-substituent desirable as "probe" for a possible delocalization of the phosphorus lone-pair of electrons in (I), as this effect should influence the ^{13}C chemical shifts and ^{13}C-^{31}P couplings of this substituent.

The ^{13}C NMR parameters (listed in Table 1) were obtained from single scan natural abundance ^{13}C spectra (Figure 1) recorded on a Varian XL-100-15 spectrometer (25.2 MHz, c.w.mode, ^{2}H lock, 12-mm tubes) using noise and single-frequency proton decoupling. Line positions were determined from spectra having a sweep width of 0.5 Hz/cm.

The assignments and signs of the ^{13}C-^{31}P coupling constants in (I), (II), and (III) were obtained using the selective and off-resonance proton decoupling techniques recently described [8a] taking into account the signs and magnitudes of $^{2}J_{P-H(2)}$ and $^{3}J_{P-H(3)}$ in phospholes, 2-phospholenes, and vinylphosphines (for all compounds $^{2}J_{P-H(2)}$ and $^{3}J_{P-H(3)}$ were shown to have the same sign, taken to be positive as in trivinylphosphine [9]). For the phenyl-substituents the coupling assignments and signs followed as described for triphenylphosphine [8c]. Full experimental details will be given in a subsequent paper on ^{13}C NMR studies of substituted phospholes.

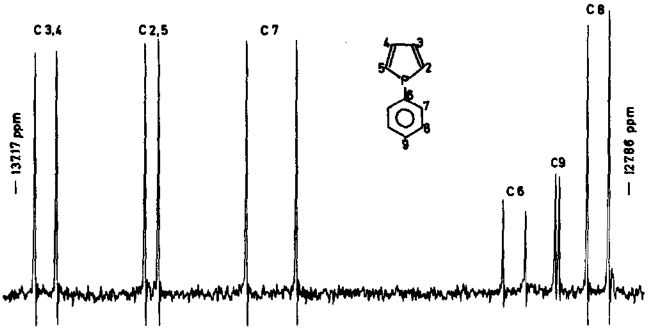
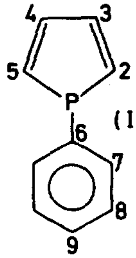


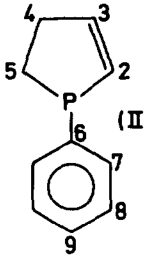
Figure 1. Single scan natural abundance proton-decoupled ^{13}C NMR spectrum of 1-phenylphosphole (I). The ppm scale is downfield from internal TMS

Comparison of the ^{13}C NMR parameters in Table 1, with the purpose of obtaining evidence, if any, for electron delocalization ("aromaticity") in (I), shows several interesting features. In view of the recently reported orientational effect of lone-pair electrons on two-bond $^{2}J_{CCP}$ couplings, as observed in aromatic and heteroaromatic phosphines [8d] and in some four-membered cyclic phosphines [10], the large variations observed for the magnitudes of $^{3}J_{C(3)-P}$ in (I), (II), and (III) appear to reflect the preferred conformations expected for the C(3)-C(2)-P-X (X = lone-pair of electrons) moiety in these compounds. According to this model [8d,10], $^{3}J_{C(3)-P}$ should reach its maximum and minimum values at C(3)-(2)-P-X dihedral angles of ~ 0° and 180°, resp. In fact, the predicted conformations (dihedral angles) in (II)[7b] and (III) agree with the observed magnitudes of $^{3}J_{C(3)-P}$. The increase observed for $^{3}J_{C(3)-P}$ in going from (II) to (I) thus probably corresponds to a decrease in the average dihedral C-C-P-X angle, resulting from lowering of the barrier to pyramidal inversion at phosphorus in phospholes [5a-b,7b]. This lowering of barrier height (to ~ 15-16 kcal/mole) was recently suggested as a measure of phosphole aromaticity [5a-b,7b],

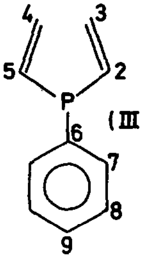
TABLE 1. ^{13}C Chemical Shifts and ^{13}C-^{31}P Coupling Constants in 1-Phenylphosphole (I), 1-Phenyl-2-phospholene (II), Divinylphenylphosphine (III) and Triphenylphosphine (IV).[a]



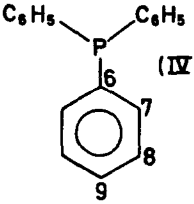
(I)



(II)



(III)



(IV)

δ C(2)	135.11	129.31	136.95	
δ C(3)	136.71	142.93	128.10	
δ C(4)	136.71	34.21	128.10	
δ C(5)	135.11	25.90	136.95	
δ C(6)	129.59	140.64	137.31	54.97[b] (137.39)
δ C(7)	133.31	131.84	132.32	58.65[b] (133.71)
δ C(8)	128.33	128.23	128.48	63.85[b] (128.51)
δ C(9)	128.95	128.35	128.56	63.71[b] (128.65)
$^{1}J_{C(2)-P}$	- 5.18	-16.03	-13.91	
$^{2}J_{C(3)-P}$	+ 8.17	+ 1.87	+23.16	
$^{2}J_{C(4)-P}$	+ 8.17	5.37[c]	+23.16	
$^{1}J_{C(5)-P}$	- 5.18	-10.24	-13.91	
$^{1}J_{C(6)-P}$	- 8.63	25.87[d]	9.17[d]	-12.51
$^{2}J_{C(7)-P}$	+19.09	+18.54	+18.70	+19.65
$^{3}J_{C(8)-P}$	+ 8.29	+ 6.32	+ 6.74	+ 6.80
$^{4}J_{C(9)-P}$	1.43[c]	0.61[d]	0.48[c]	0.33[d]

[a] Solutions are ca. 65% w/w in $(CD_3)_2CO$ (28% w/w) and TMS (7% w/w) except for (IV): 36% w/w in CS_2 (52% w/w) and $(CD_3)_2CO$ (12% w/w)[8c]. Chemical shifts are in ppm downfield from internal TMS with errors ±0.01 ppm; coupling constants are in Hz with errors ±0.03 Hz.

[b] In ppm upfield from internal CS_2 [8c]; values in parentheses are after conversion to the TMS scale.

[c] Sign opposite to that of the corresponding ring ^{1}H-^{31}P coupling constant.

[d] Sign not obtained.

which thus appears also to be reflected by the magnitude of $^{2}J_{C(3)-P}$ in these systems.

It is observed that phosphole aromaticity as depicted from barrier heights to phosphorus inversion has a profound influence on the chemical shift of C(6) which is more than 10 ppm more shielded than in (II). Furthermore, the small increase observed for $^{1}J_{C(2)-P}$ in (I) may also be taken as evidence for some degree of electron delocalization. Finally, it should be noted that the reversal of the chemical shift order for C(2) and C(3) in going from (III) to (II), and even the chemical shifts themselves in (II), are extremely well predicted using the substituent parameters reported by Stothers [11]. A more detailed discussion of the small changes observed for the other parameters in Table 1 will have to await the results of the ^{13}C NMR studies of other substituted phospholes presently being studied.

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