Density Functional Theory (DFT) Calculations of Indirect Nuclear Spin-Spin Coupling Constants $^1J(^{31}P, ^{13}C)$ in λ^3-Phosphaalkynes

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The calculation of the spin-spin coupling constants $^1J(^{31}P,\equiv^{13}C)$ of λ^3-1-phosphaalkynes P≡C-R (R = H, Me, ^{t}Bu, Ph, SiMe$_3$ and NMe$_2$) using density functional theory (DFT) have revealed a positive sign of this coupling constant in agreement with the experiment for P≡C-^{t}Bu. The calculations have shown that the Fermi contact (FC) contribution to this coupling is negative [in contrast to FC for $^1J(^{14}N,\equiv^{13}C)$ in the corresponding nitriles], and that the positive sign of $^1J(^{31}P,\equiv^{13}C)$ is the result of significant contributions arising from spin-dipole (SD) and paramagnetic spin-orbital (PSO) terms. Coupling constants were also calculated for some representative λ^3-phosphorus compounds containing two- and three-coordinate phosphorus, indicating the strong dependence of the FC term on the geometry at the phosphorus atom.

Key words: Phosphaalkynes, NMR, Coupling Signs, MO Calculations

Introduction

The convenient synthesis of *tert*-butylphosphaalkyne P≡C-^{t}Bu [1] and of kinetically unstabilized phosphaalkynes [2] has opened an amazingly fruitful field of phosphorus chemistry [3, 4]. Although numerous NMR parameters of phosphaalkynes have been reported [1, 2, 5], the interpretation of the data, especially of the coupling constants $^1J(^{31}P,\equiv^{13}C)$, is not straightforward. The comparison of chemical shifts of phosphaalkynes ($\delta^{13}C$, $\delta^{31}P$) and alkynes ($\delta^{13}C$) reveals similar trends [4b, 6], and there is a crudely linear correlation between $\delta^{31}P$ of phosphaalkynes and $\delta^{15}N$ of analogous nitriles [7]. It appears that there is also a correlation between coupling constants $^1J(^{31}P,\equiv^{13}C)$ and $^1J(^{15}N,\equiv^{13}C)$ for these compounds [7]. A positive sign of $^1J(^{31}P,\equiv^{13}C)$ in P≡C-^{t}Bu has been determined experimentally [8]. This is an intriguing result, since the experimental evidence available for almost all other organophosphorus compounds shows that $^1J(^{31}P, ^{13}C)$ possesses a negative sign if a lone pair of electrons is present at the phosphorus atom [9, 10]. In the present work, we report on non-empirical calculations of $^1J(^{31}P,\equiv^{13}C)$ of phosphaalkynes in comparison with calculated data $^1J(^{15}N,\equiv^{13}C)$ of corresponding nitriles.

The theory of electron-mediated (indirect) nuclear spin-spin coupling (*J*-coupling) [11] shows that three mechanisms have to be considered: the Fermi contact term (FC), the spin-dipole term (SD) and the spin-orbital term (SO). The latter is the sum of diamagnetic (DSO) and paramagnetic (PSO) contributions, of which the DSO contribution is very small and can be neglected for the present purpose. Dealing with single bonds, the contribution of the FC term is generally assumed to dominate, with the exception of couplings in which ^{19}F is involved [12]. In the case of multiple bonding, it is expected that the importance of both the SD and SO terms increases [10, 11, 13]. Multiple bonding involving heavy elements, including phosphorus, has been in the centre of interest for the last three decades. Since there is no way to determine the relative contributions to *J*-coupling by experiments, all discussions have to be based on calculations. The improving performance of MO calculations, in particular those using DFT methods, raises the hope that *J*-couplings can be calculated to yield magnitude and sign in close agreement with experimental data [14, 15]. This has been shown for $^1J(^{11}B,^1H)$, $^1J(^{11}B,^{11}B)$ and $^1J(^{13}C,^{11}B)$ of polyhedral boron hydrides and carboranes [16] and for $^1J(^{13}C,^{13}C)$ of numerous cyclic compounds [17, 18], to name just a few successful applications. For *J*-coupling involving ^{31}P the accuracy of the calculated data will certainly be lower than for lighter nuclei. Nevertheless the calculations can provide information on trends, in

Table 1. Calculated and experimental ^{31}P NMR parameters[a] of phosphaalkynes and ^{14}N NMR parameters[b] of nitriles[c].

	δ^{31}P/ δN (exp.)	δ^{31}P/ δN (calc.)	$^1J(^{31}$P,$\equiv^{13}$C)/ $^1J(^{14}$N,$\equiv^{13}$C) (exp.)	$^1J(^{31}$P,$\equiv^{13}$C)/ $^1J(^{14}$N,$\equiv^{13}$C) (calc.)	^{31}P$\equiv^{13}$C/ ^{14}N$\equiv^{13}$C FC (calc.)	^{31}P$\equiv^{13}$C/ ^{14}N$\equiv^{13}$C SD (calc.)	^{31}P$\equiv^{13}$C/ ^{14}N$\equiv^{13}$C PSO (calc.)
H-C≡P	−32.0	−15.0	(+)54.0	+64.0	−21.0	+63.0	+22.0
H-C≡N[d]	−120.0	−101.7	+13.2	+16.3	+11.5	+4.4	+0.4
Me-C≡P[e]	−60.0	−38.0	(+)49.0	+54.1	−26.8	+59.7	+21.1
Me-C≡N	−136.0	−122.3	+12.5	+14.6	+10.1	+4.2	+0.3
^{t}Bu-C≡P[f]	−69.0	−41.3	+38.5	+41.1	−35.2	+58.1	+18.0
^{t}Bu-C≡N	−139.0	−127.5	+10.7	+12.5	+8.3	+4.1	+0.1
Ph-C≡P	−32.0	+8.6	(+)48.3	+51.4	−24.6	+58.1	+17.8
Ph-C≡N	−121.5	−97.9	−	+14.1	+9.88	+4.2	+0.1
Me$_3$Si-C≡P	+96.0	+140.8	(+)13.9	+20.0	−36.8	+55.9	+0.8
Me$_3$Si-C≡N	−77.7	−67.5	+8.3	+10.3	+7.4	+4.0	−1.0
Me$_2$N-C≡P[g]	−137.6	−108.4	(+)18.2	+8.1	−67.5	+50.1	+25.4
Me$_2$N-C≡N	−176.3[h]	−162.6	−	+13.2	+8.4	+3.9	+0.8

[a] Calculated $\sigma(^{31}$P) data are converted to δ^{31}P data by δ^{31}P $= \sigma(^{31}$P) [PH$_3$]$-\sigma(^{31}$P) $- 266.1$, with $\sigma(^{31}$P) [PH$_3$] $= +563.2$, δ^{31}P[PH$_3$]$= -266.1$ and δ^{31}P [H$_3$PO$_4$ (aq, 85%)] $= 0$ [24]; [b] calculated σ(N) data are converted to δN data by δN$= \sigma$(N)[NH$_3$] $- \sigma$(N) $- 399.3$, with σ(N) [NH$_3$] $= 259.4$, δN [NH$_3$]$= -399.3$ and δN [neat MeNO$_2$]$= 0$ [25]; [c] experimental data: see [7] and references cited therein, if not stated otherwise; [d] $^2J(^{31}$P,^{1}H) (exp.) $= 44.0$ [2]; (calc.) $+ 47.8$ Hz (FC: $+18.6$; SD: $+4.4$; PSO: $+25.8$); [e] $^2J(^{31}$P,^{13}C) (exp.) $= 20.0$ [2]; (calc.) -21.1 Hz (FC: -18.5; SD: $+0.7$; PSO: -3.2); $^3J(^{31}$P,^{1}H) (exp.) $= 15.0$ [2]; (calc.) $+8.8$ Hz; [f] $^2J(^{31}$P,^{13}C) (exp.) $= 18.2$ [1]; (calc.) -19.4 Hz (FC: -17.3; SD: $+0.9$; PSO: -2.9); there is a misprint in ref. [8]: the experimental sign of $^2J(^{31}$P,^{13}C) is negative; $^3J(^{31}$P,^{13}C) (exp.) $= 6.0$ [1]; (calc.) $+3.1$ Hz; $^4J(^{31}$P,^{1}H) (exp.) $= +0.9$ [8]; (calc.) $+0.5$ Hz; [g] experimental data for Me$_3$Si(^{i}Pr)N-C≡P [5a, d]; calculated data depend on substituents at nitrogen: e.g. Me(H)N-C≡P: δ^{31}P -105.7; $^1J(^{31}$P,$\equiv^{13}$C) $+17.3$ Hz (FC: -61.7; SD: $+51.5$; PSO: $+27.3$); and H$_2$N-C≡P: δ^{31}P -120.9; $^1J(^{31}$P,$\equiv^{13}$C) $+26.8$ Hz (FC: -58.1; SD: $+54.3$; PSO: $+31.2$); [h] M. Witanowski, W. Sicinska, Z. Biedrzycka, G. A. Webb, J. Mol. Struct. **380**, 133 (1996).

Table 2. Calculated[a] and experimental ^{31}P NMR parameters of two- and three-coordinate λ^3-phosphorus and corresponding nitrogen compounds[b].

	δ^{31}P/ δN (exp.)	δ^{31}P/ δN (calc.)	$^1J(^{31}$P,^{13}C)/ $^1J(^{14}$N,^{13}C) (exp.)	$^1J(^{31}$P,^{13}C)/ $^1J(^{14}$N,^{13}C) (calc.)	^{31}P^{13}C/ ^{14}N^{13}C FC (calc.)	^{31}P^{13}C/ ^{14}N^{13}C SD (calc.)	^{31}P^{13}C/ ^{14}N^{13}C PSO (calc.)
Me$_3$P	−63.3	−60.0	−13.6	−37.5	−49.3	+6.2	−2.8
Me$_3$N	−363.1	−360.3	(+)2.1[c]	+2.1	+2.0	+0.4	−0.3
PH$_3$	−266.1	−266.1	+186.4 (P−H)	+136.5	+131.6	−1.0	+5.8
NH$_3$ (gas phase)	−399.3	−399.3	+43.6 (N−H)	+42.1	+39.8	+0.2	+2.0
Phosphabenzene[d]	+211.0	+243.2	(−)53.0	−84.6	−49.3	+6.2	−41.7
Pyridine	−63.2	−39.1	−0.5	−0.8	+3.0	+0.4	−4.2
1-Me-1-phosphole[e]	−8.7	−32.3	(−)7.0 (P-C=)	−15.2	−0.3	+1.7	−14.2
1-Me-pyrrole	−230.1	−224.8	+9.3 (N-C=)	+10.0	+12.6	+0.2	−2.5
1,3-Me$_2$-1,2,5-diazaphosphole[f]	+231.0 (P-5)	268.5	−34.8	−59.0	−25.1	+6.5	−40.7
	−146.7 (N-1)	−118.7	−55.7(P-N(1))	−69.8	−54.7	+2.0	−17.2
	−13.7 (N-2)	+19.6	−6.3 (P-N-N(2))	−7.5	−2.2	+4.2	−9.5
P$_4$ (gas phase)	−553.1	−569.9	−	−192.8 (P-P)	−167.3	−5.9	−19.9

[a] See footnotes [a] and [b] in Table 1; [b] experimental data taken from S. Berger, S. Braun, H.-O.Kalinowski, NMR Spectroscopy of the Non-Metallic Elements, Wiley, Chichester, 1997 if not noted otherwise; [c] data taken for quinuclidine; [d] other coupling constants in Hz: exp. [26] (calc.) $^2J(^{31}$P,^{13}C) $= 14.0$ ($−13.3$), $^3J(^{31}$P,^{13}C) $= 22.0$ ($+20.5$), $^2J(^{31}$P,^{1}H) $= 38.0$ ($+42.0$); $^3J(^{31}$P,^{1}H) $= 8.0$ ($+5.0$); $^4J(^{31}$P,^{1}H) $= 3.5$ ($−2.3$); [e] the calculated coupling constant $^1J(^{31}$P,^{13}C=) is extremely sensitive to the geometry at the phosphorus atom; a planar phosphole structure gives the following calculated data: $^1J(^{31}$P,^{13}C=) $+102.3$ Hz (FC: $+122.6$; SD: $+1.6$; PSO: $−22.3$); [f] coupling constants and signs [27].

particular with respect to contributions arising from the different coupling mechanisms. The results for phosphaalkynes and nitriles are listed in Table 1. Table 2 contains calculated data for some other representative two- and three-coordinate λ^3 phosphorus compounds.

The correlation between calculated shielding $\sigma(^{31}P)$ ([19] GIAO-RB3LYP/6-311+G(d,p)) and experimental chemical shifts $\delta^{31}P$ is close to linear with a slope of about -1 and an intercept of about 280 ppm (data for compounds in Tables 1 and 2 and others, not included in this work). This indicates that the optimised gas phase geometries (RB3LYP/6-311+G(d,p) [20]) are approximately correct and agree with the molecular structures in solution. The calculated magnitudes of the coupling constants $^{1}J(^{31}P,\equiv^{13}C)$ and $^{1}J(^{14}N,\equiv^{13}C)$ are in reasonable agreement with the experimental data, and the experimentally determined coupling signs are reproduced quite well (Table 1). It is important to note that the FC contribution to $^{1}J(^{31}P,\equiv^{13}C)$ is negative as in most other organophosphorus compounds bearing a lone pair of electrons at the phosphorus atom. The positive sign of $^{1}J(^{31}P,\equiv^{13}C)$ results mainly from significant positive SD contributions. The PSO contribution is smaller in each case and also positive, at least for H-C≡P, Me-C≡P and ^{t}Bu-C≡P, whereas the PSO contribution for Me$_3$Si-C≡P becomes close to zero. The same trend of the SD and PSO contributions can be seen by inspecting the data for the nitriles. The magnitude of these contributions is much reduced when compared with the phosphaalkynes because of the smaller magnetic moment of the ^{14}N nucleus $[\gamma(^{31}P)/\gamma(^{14}N) = 5.61]$, and because of the differences in the electronic structures of nitriles and phosphaalkynes [21]. The latter influence becomes apparent by comparing the signs of the FC contributions: in the case of the phosphaalkynes, the FC contribution is negative as the result of the high s-character of the lone pair of electrons, in contrast to the nitriles where the FC contribution is still positive in spite of the presence of the lone pair of electrons at the nitrogen atom.

The sensitivity of the FC term to molecular structure and the nature of the lone pair is demonstrated by the data in Table 2. The agreement between calculated and experimental data is less convincing for Me$_3$P, phosphabenzene, or phosphole. In contrast to the situation of the linear phosphaalkynes, any change in the CPC bond angle has a fairly large effect on the FC contribution. An extreme case is the structure of phospholes which are non-planar in the ground state and planar in

the excited state [22]. The calculated data in Table 2 (see also footnote [d]) for both geometries indicate a large positive FC contribution to $^{1}J(^{31}P,^{13}C)$ for the planar structure in contrast to the small and negative FC contribution for the non-planar structure. In the planar structure, the lone pair of electrons at the phosphorus atom has lost most of its s character and is part of the heteroaromatic system.

The PSO term results from B_0-induced paramagnetic electron currents in the valence orbitals, and it may become significant if occupied and virtual orbitals (those which have marked p or d character) are close in energy. The sign of the PSO contribution can be positive, as for most couplings between nuclei participating in triple bonds (see HC≡CH [15a], and Table 1) or negative as for nuclei in double bonds (see H$_2$C=CH$_2$ [15a], and Table 2).

The SD term may become important (similar to PSO) if occupied and virtual p orbitals, close in energy, are present, typical of multiple bonds, in particular of triple bonds, as shown by the calculated SD contributions in the Tables 1 and 2.

Experimental Section

All calculations were performed using the Gaussian 03 package [23]. The gas phase geometries were optimised with DFT methods (B3LYP) [20a] and the 6-311+G(d,p) basis set [20b, c]. As expected [12, 14, 15], HF calculations of the coupling constants gave poor results when compared with the B3LYP method. The calculations provide the magnitude of the spin-spin coupling constants in Hz as well as the contributions from the FC, SD and SO terms for the ^{1}H, ^{13}C, ^{14}N and ^{31}P nuclei which all possess a positive gyromagnetic ratio γ. Coupling constants involving ^{15}N $[\gamma(^{15}N) = -2.7126]$ can be compared if the respective data in the Tables 1 and 2 are multiplied by the factor -1.403 corresponding to $\gamma(^{15}N)/\gamma(^{14}N)$. Tables 1 and 2 list the paramagnetic spin-orbital (PSO) contribution; the diamagnetic spin-orbital (DSO) contribution was < 1 Hz in all cases studied.

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