

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

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The calculation of the spin-spin coupling constants $^1J(^{31}\text{P}, ^{13}\text{C})$ of λ^3 -1-phosphaalkynes $\text{P}\equiv\text{C}-\text{R}$ ($\text{R} = \text{H}, \text{Me}, ^t\text{Bu}, \text{Ph}, \text{SiMe}_3$ and NMe_2) using density functional theory (DFT) have revealed a positive sign of this coupling constant in agreement with the experiment for $\text{P}\equiv\text{C}-^t\text{Bu}$. The calculations have shown that the Fermi contact (FC) contribution to this coupling is negative [in contrast to FC for $^1J(^{14}\text{N}, ^{13}\text{C})$ in the corresponding nitriles], and that the positive sign of $^1J(^{31}\text{P}, ^{13}\text{C})$ 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