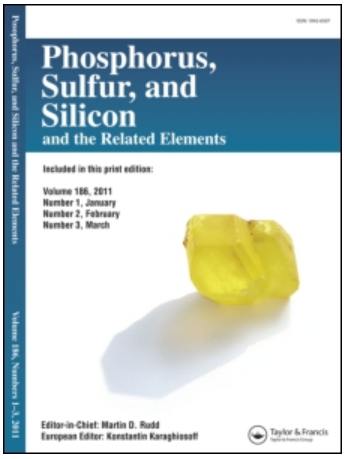

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15^{N}, 31^{P}, and ^{13}C NMR Spectroscopy of N-Arylsulfonyl-and N-Arylcarbonyl-P,P,P-triphenylphospha-λ-Azenes. Substituent Effects and Electronic Structure

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^{15}N, ^{31}P, and ^{13}C NMR Spectroscopy of N-Arylsulfonyl- and N-Arylcarbonyl-P,P,P-triphenylphospha-λ^5-Azenes. Substituent Effects and Electronic Structure

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The ^{15}N, ^{31}P and ^{31}C NMR spectra of several series of phospha-λ^5-azenes are reported. For the N-arylsulfonyl-P,P,P-triphenylphospha-λ^5-azene series (R-C_6H_4-SO_2-N=PPh_3), the ^{31}P chemical shifts, various ^{13}C chemical shifts and $^1J_{PN}$ were observed to correlate linearly with the Hammett σ constants. Interestingly, the ^{15}N chemical shifts did not correlate acceptably with any σ or with the Taft dual substituent parameter equation, and $^1J_{PC}$ was invariant with substituent. For the N-arylcarbonyl-P,P,P-triphenylphospha-λ^5-azene series (R-C_6H_4-CO-N=PPh_3), $\delta_{^{31}P}$ and various $\delta_{^{13}C}$'s were observed to linearly correlate with the σ constants, while $\delta_{^{15}N}$, $^1J_{PN}$ and $^1J_{PC}$ correlated with both the σ and σ^- constants. For the N-phenyl-P,P,P-triarylphospha-λ^5-azene series [Ph-N=P(C_6H_4-R)$_3$] the best correlations were observed between ^{31}P, ^{15}N and several ^{13}C chemical shifts and the σ constants. However, $^1J_{PN}$ correlated with both σ^- and σ while $^1J_{PC}$ correlated with σ_R and, interestingly, the slope of these correlations had the same sign. These data will be discussed in terms of inductive and resonance effects and the contribution of pπ-dπ and pπ-σ^* bonding to the phosphazene system. These results will be compared to those in the N-aryl-P,P,P-triphenyl-phospha-λ^5-azene series (R-C_6H_4-N=PPh_3) where the chemical shifts (^{15}N, ^{31}P and ^{13}C) and $^1J_{PC}$ were observed to correlate with σ^- while $^1J_{PN}$ correlated with σ_R and σ_R^+. In this case it was suggested that the chemical shifts were sensitive to electron density rather than to pπ-dπ bonding and that the coupling constant changes could be understood in terms of both pπ-dπ PN bonding and competitive pπ-σ^* bonding.