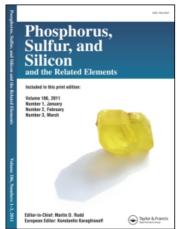
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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: <a href="http://www.informaworld.com/smpp/title~content=t713618290">http://www.informaworld.com/smpp/title~content=t713618290</a>

# Transmission of Molecular Structure on NMR Characteristics of Phosphorus-Nitrogen Double Bond Systems

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**To cite this Article** Gudat, Dietrich , Niecke, Edgar , Grossmann, Gisbert and Krüger, Kerstin(1999) 'Transmission of Molecular Structure on NMR Characteristics of Phosphorus-Nitrogen Double Bond Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 147: 1, 103

To link to this Article: DOI: 10.1080/10426509908053532 URL: http://dx.doi.org/10.1080/10426509908053532

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## Transmission of Molecular Structure on NMR Characteristics of Phosphorus-Nitrogen Double Bond Systems

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Elucidation of the origin for the large variability of <sup>31</sup>P and <sup>15</sup>N chemical shifts in compounds with P-N double bonds is a challenging task. We demonstrate here how trends in <sup>31</sup>P and <sup>15</sup>N chemical shifts of iminophosphines and ylene-iminophosphoranes can be explained by the use of quantum chemical model concepts.

- Iminophosphines RO-P=NMes\* display large variations of molecular geometries [1]. A characterization of <sup>31</sup>P shielding tensors of five derivatives by CP-MAS experiments and model calculations clearly confirms a gradual change in P-N bond order from a formal double to a triple bond which follows closely the geometry deformations [2].
- $\sim \delta^{15}N$  in ylene-imino-phosphoranes X-P(=Y)=NR is influenced according to model calculations by both substituent effects and E/Z-isomerism of the double bond. Comparison of <sup>15</sup>N shifts with model data revealed that in solution all P-N double bonds exhibit Z-configuration, and variations result alone from substituent effects. A correlation between  $\delta^{15}N$  and calculated bond polarities  $\Delta q = [q(P) q(N)]$  suggests that increased nitrogen shieldings indicate enhanced ylide character of P-N double bonds [3].
- The Marked changes of  $\delta^{31}$ P in compounds R-P(=Y)=NMes\* arise according to model calculations from sterically induced deformations of nitrogen valence angles, while P=N-Aryl-π-conjugation is negligible. This hypothesis is experimentally confirmed by the low barrier for N-Mes\* rotation in Mes\*P(=NH)=NMes\* (ΔH ≠ 13 kcal/mol, ΔS ≠ -12 e.u.). In addition to providing detailed insight in the electronic structures of the studied compounds, the presented results emphasize that skeletal distortions are frequently of similar importance for the interpretation of  $\delta^{31}$ P chemical shifts as electronic effects.

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