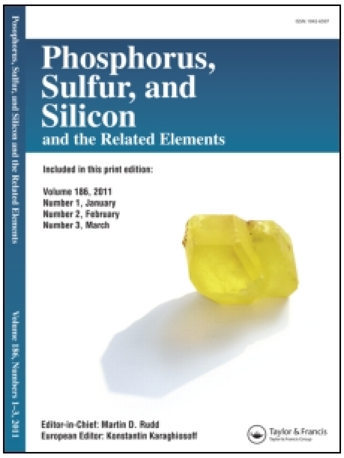

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Dietrich Gudat[a][b]; Edgar Niecke[a][b]; Gisbert Grossmann[a][b]; Kerstin Krüger[a][b]
[a] Institut für Anorganische Chemie der Universität Bonn, Bonn, Germany [b] Institut für Analytische Chemie der Universität Dresden,

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

Phosphorus, Sulfur and Silicon, 1999, Vol. 147, pp. 103-103
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

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

DIETRICH GUDAT, EDGAR NIECKE, GISBERT GROSSMANN and KERSTIN KRÜGER

Institut für Anorganische Chemie der Universität Bonn, 53121 Bonn, Germany;
Institut für Analytische Chemie der Universität Dresden

Elucidation of the origin for the large variability of ^{31}P and ^{15}N chemical shifts in compounds with P-N double bonds is a challenging task. We demonstrate here how trends in ^{31}P and ^{15}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 ^{31}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].

☞ $\delta^{15}N$ 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 ^{15}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].

☞ 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* ($\Delta H^{\neq}$ 13 kcal/mol, $\Delta S^{\neq}$ -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 ^{31}P chemical shifts as electronic effects.

References

[1] E. NIECKE, R. DETSCH, M. NIEGER, F. REICHERT, W.W. SCHOELLER, *Bull. Soc. Chim. Fr.* **1993,** *130,* 25.
[2] D. GUDAT. E. NIECKE, G. GROSSMANN, K. KRÜGER, submitted.
[3] D. GUDAT, E. NIECKE, A. RUBAN, V.V.D. GÖNNA, *Magn. Res. Chem.* **1996,** *34,* 799.