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Ab Initio Calculations Show How ^{31}P NMR Chemical Shifts in PXYZ Phosphines Correlate with Substituent Electronegativity

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AB INITIO CALCULATIONS SHOW HOW ^{31}P NMR CHEMICAL SHIFTS IN PXYZ PHOSPHINES CORRELATE WITH SUBSTITUENT ELECTRONEGATIVITY.

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Letcher and Van Wazers suggestion[1] that the ^{31}P NMR chemical shifts of phosphines might be related to the substituent electronegativity, $\text{EN}(\text{X})$ [2], has not been verified subsequently by the available experimental data[3,4]. We now have explored this relationship systematically by means of reliable[5] *ab initio* magnetic property calculations[6] on a comprehensive set of molecules: PXY_2 ($\text{Y} = \text{H}, \text{F}, \text{CH}_3, \text{Cl}$) and PXYZ ($\text{Y} = \text{H}, \text{Cl}$ and $\text{Z} = \text{F}$) with $\text{X} = \text{H}, \text{CH}_3, \text{NH}_2, \text{OH}, \text{F}, \text{SiH}_3, \text{PH}_2, \text{SH}, \text{Cl}$.

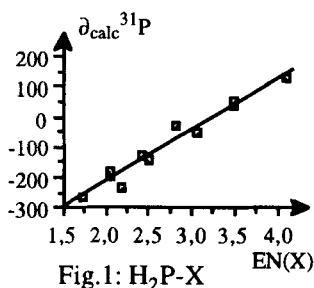


Fig.1: $\text{H}_2\text{P}-\text{X}$

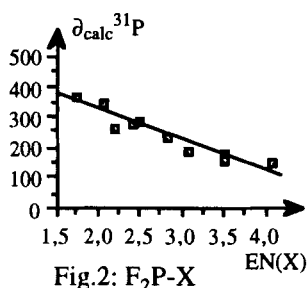


Fig.2: $\text{F}_2\text{P}-\text{X}$

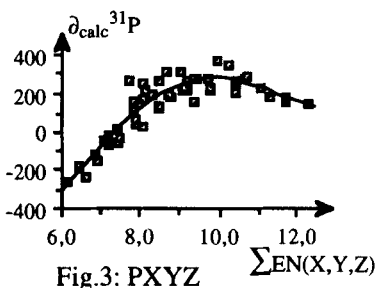


Fig.3: PXYZ

$\delta_{\text{calc}}^{31}\text{P}$ of monosubstituted phosphines, PH_2X (Fig. 1), correlates with $\text{EN}(\text{X})$ as do

those for the difluorophosphines, PF_2X (Fig. 2). However, the slopes are opposite !

Data for a more varied set of phosphines, PXYZ , when plotted against the electronegativity sum, $\Sigma\text{EN}(\text{X},\text{Y},\text{Z})$, reveals a general pattern (Fig. 3) which combines both these trends.

Using a simple MO model, Letcher and VanWazer predicted similar behavior for hypothetical PX_3 models with increasing $\Sigma\text{EN}(\text{X},\text{Y},\text{Z})$ from 3.0 to 12.0 .[1]

[1] J. H. Letcher ; J. R. Van Wazer, *J. Chem. Phys.*, **44**, 815 (1966).

[2] Substituent electronegativity defined by the Allred-Rochow electronegativity of the attached substituent atom.

[3] A. Schmidpeter; H. Brecht, *Z. Naturforsch.*, **24b**, 179 (1969).

[4] *Phosphorus to Bismuth*; K.R. Dixon, Ed.; Plenum Press: New York, 1987, pp 369.

[5] D.B. Chesnut; B.E. Rusiloski, *Chem. Phys.*, **157**, 105 (1991).

[6] $\delta_{\text{calc}}^{31}\text{P}$: SOS-MBPT/BIII //RMP2/6-31+G** with DeMon93© and GAUSSIAN92©.