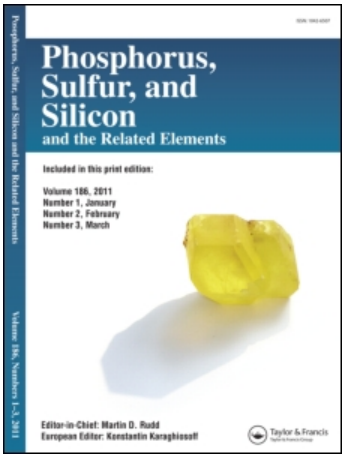

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Ab Initio Calculations Show How ^{31}PNMR Chemical Shifts in PXYZ Phosphines Correlate with Substituent Electronegativity

A. Dransfeld[a]; P. v. R. Schleyer[a]
[a] Computational Chemistry Center of the Institute of Organic Chemistry, Erlangen-Nürnberg University, Erlangen

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

A. DRANSFELD, P.v.R. SCHLEYER
Computational Chemistry Center of the Institute of Organic Chemistry, Erlangen-Nürnberg University, Nägelsbachstraße 25, D-91052 Erlangen, FAX: +49 9131 856566

Letcher and Van Wazers suggestion[1] that the ^{31}P NMR chemical shifts of phosphines might be related to the substituent electronegativity, EN(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 (Y= H, F, CH_3, Cl) and PXYZ (Y= H, Cl and Z= F) with X= H, CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl.

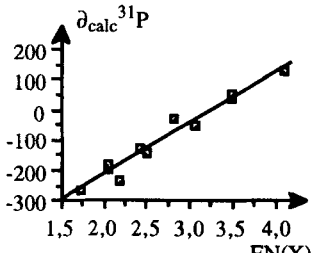

Fig.1: H_2P-X

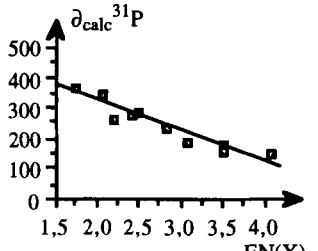

Fig.2: F_2P-X

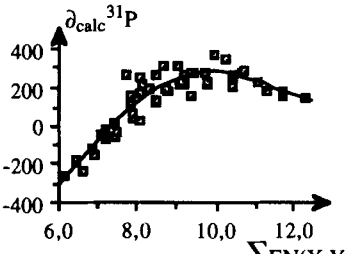

Fig.3: PXYZ

$\partial_{calc}{}^{31}P$ of monosubstituted phosphines, PH_2X (Fig. 1), correlates with EN(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, ΣEN(X,Y,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 ΣEN(X,Y,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] $\partial_{calc}{}^{31}P$: SOS-MBPT/BIII //RMP2/6-31+G** with DeMon93© and GAUSSIAN92©.