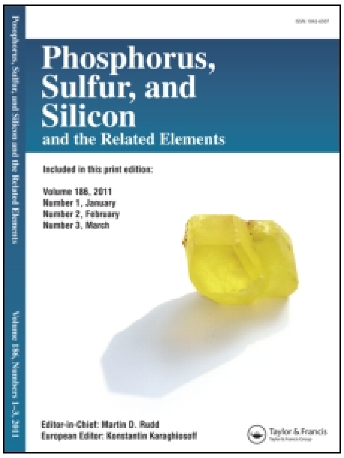

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How Does the ^{31}P NMR Chemical Shift Change with Phosphorus Bond Length? an *Ab Initio* NMR Study

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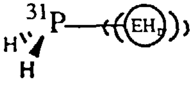
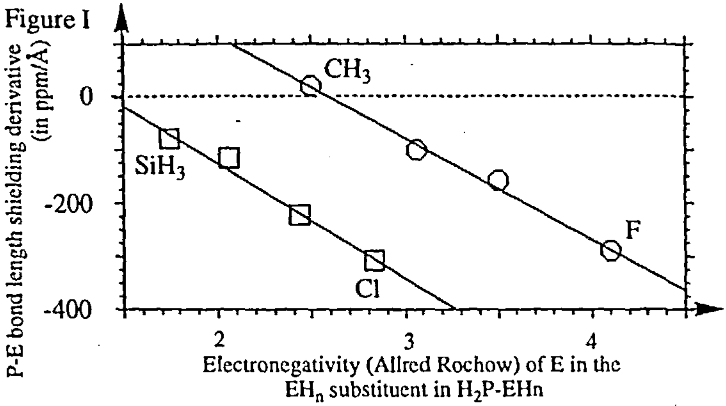
In NMR experiments it is difficult to modify the phosphorus bond length, R(P-E), by, for example, isotopic substitution or by placing the molecule in an exited rovibrational state (dynamic NMR).[1] In contrast, *ab initio* NMR computations can be performed not only for energy minimized structures but also for geometries with systematically modified bond lengths.[2] The first derivative (defined by the slope of the $\delta^{31}P$ versus R(P-E) correlation line) characterizes how sensitive the chemical shift is to bond lengthening or shortening, respectively.



Our *ab initio* results provide isotropic NMR shielding bond length derivatives based on **GIAO-MP2**[3]//RMP2(fc)/6-31+G(d) calculations.[4] The estimated infinite order many-body perturbation theory (**EMPI**) approach[5] is demonstrated to yield best agreement with experimental data. While most $H_2P\text{-}EH_n$ molecules have derivatives in agreement with the predicted 'universal shielding surface'[6], some molecules with first row substituents (EH_n= Li, BeH, BH_2) display unusual slopes which are due to the ionic character of the P-E bond or reflect the partial π bond character of the B-P bond. For group IV to VII elements a striking correlation between the electronegativity of E and the P-E bond length derivative occurs (see figure I) within each period.

Figure I



EMPI/tz2p//RMP2(fc)/6-31+G* calculated bond length derivatives of H_2P-EH_n molecules with E= CH_3, NH_2, OH, F, and SiH_3, PH_2, SH, and Cl. Correlation lines for E from first row (circles, cc: 0.994) and from second row (squares, cc:0.979).

Are bond length derivatives sufficient to describe isotope and temperature effects on the chemical shift? For simple cases this approximation may be sufficient. Nevertheless, bond bending and other internal molecular motions may also effect the average NMR shielding. Systematic deformation along the ground state vibration modes allows to *ab initio* calculate the average NMR shielding. Not all vibration modes have an effect, even if their first bond length derivative is large. For example in X-CP molecules the effect of the bond stretching mode with a large derivative is completely compensated. In contrast, vibration mode following (VMF) correction for the X-C-P bond bending changes the calculated isotropic average ^{31}P shielding by nearly 10 ppm.

References

[1] C. D. Jameson, A. C. de Dios, A. K. Jameson, J. Chem. Phys. 95 (1991) 9042.
[2] D. B. Chesnut and D. W. Wright, J. Comput. Chem. 12 (1991) 546; D. B. Chesnut, Chem. Phys. 110 (1986) 415.
[3] J. Gauss, J. Chem. Phys. 99 (1993) 3629.
[4] A. Dransfeld, D. B. Chesnut, Chem. Phys. in press, 1998.
[5] D. B. Chesnut, Chem. Phys. Lett. 246 (1995) 235.
[6] C. J. Jameson and A. C. de Dios, J. Chem. Phys. 98 (1993) 2208.