

## Molecular orbital analysis of the halogen dependence of nuclear magnetic shielding in $PX_3$ and $POX_3$ ( $X = F, Cl, Br, I$ )

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**Abstract:** Nuclear magnetic resonance (NMR) spectroscopy analyzes the magnetic properties of an active nucleus for physical and chemical determination. Important information about chemical bonding and molecular structure are provided by chemical shifts ( $\delta$ ) and spin-spin coupling parameters.[1,2] The chemical shift ( $\delta$ ) trends for halogen (X) in different nuclei ( $^{125}Te$ ,  $^{13}C$ ,  $^{139}La$ ,  $^{31}P$ , etc.) have been investigated experimentally and theoretically.[2] Chemical shift behaves quite differently among some isotopes, i.e., for  $^{13}C$  ( $CX_4$ ) it decreases strongly along the series ( $X=F, Cl, Br, I$ ), namely normal halogen dependence (NHD); on the other hand,  $^{139}La$  ( $LaX_3$ ) chemical shift increases strongly, showing an inverse halogen dependence (IHD).[3-5]  $PX_3$  series shows an IHD while its oxide form,  $POX_3$ , presents NHD. The halogen dependence on  $^{31}P$  was investigated by density functional theory (DFT) calculations and natural localized molecular orbitals (NLMO)[6] using the Amsterdam density functional (ADF, v. 2014) software. Geometry optimization and  $^{31}P$  NMR shielding tensor calculations were performed using PBE0 hybrid functional and TZ2P basis set.[7-9] The shielding tensors were decomposed into paramagnetic ( $\sigma_{para}$ ), diamagnetic ( $\sigma_{dia}$ ) and spin-orbit ( $\sigma_{so}$ ) contributions and their principal components were obtained. Only  $\sigma_{para}$  and  $\sigma_{so}$  contributions change along the series, in which the magnitude of  $\sigma_{para}$  component is always larger than the  $\sigma_{so}$ . The negative  $\sigma_{para}$  tensor has the largest changes in comparison with the positive  $\sigma_{so}$  one, explaining IDH for  $PX_3$  series. The  $\sigma_{para}$  decomposition component showed that  $\sigma P-X$  and  $LP-P$  NLMOs have the largest contribution. These two orbitals correspond to about 70% of the  $\sigma_{para}$  total value. For the  $POX_3$  series, the positive  $\sigma_{so}$  tensor has the largest variation, leading to NDH for these oxide phosphines. The  $\sigma P-X$ ,  $\sigma P-O$ ,  $CR_2-P$ ,  $\sigma^* P-X$  and  $\sigma^* P-O$  NLMOs have the largest contribution to  $\sigma_{so}$  tensor. The  $\sigma_{so}$  tensor increase may be understood as interaction between the SO coupling of the heavy atom (HA) and the spin-dependent fermi contact (FC) and spin-dipolar (SD) mechanisms. The induced spin polarization can be transmitted through a covalent bond from an HA (halide) to an LA (neighboring phosphorus) nucleus, resembling the transmission mechanism of the FC term in indirect spin-spin coupling constants (FC/FC mechanism).[10,11] The  $s$  and  $p$  character of the  $\sigma P-X$  bond influences the components  $\sigma_{para}$  and  $\sigma_{so}$ . The  $PX_3$  series shows an increase of  $p$ -character and subsequent decrease of  $s$ -character in both P and X atoms of the  $\sigma P-X$  bond, whereas in the  $POX_3$  series the  $s$ - and  $p$ -character are almost constant, with values of 40 and 60% respectively. This result may be one evidence among others that NDH and IDH effects are associated mainly with  $s$ - and  $p$ -character, respectively.



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