

The Electron Localization Function (ELF) Description of the PO Bond in Phosphine Oxide

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The electron localization function^{1–5} (ELF) has been used to study the disposition of electron pairs in H₃PO. Three attractors corresponding to lone pairs on the oxygen are found behind the oxygen (away from phosphorus) staggered with respect to the PH bonds. The nature of the isosurfaces for the lone pairs and the PO bond attractor is indicative of an ionic type of environment around oxygen and supportive of the oxygen lone pair polarization and back-bonding stabilization of the PO bond.

The nature of the bonding in the PO bond of phosphine oxides (R₃PO) has been of great interest for many years. It has been reviewed extensively by Gilheany^{6,7} who points out that both experiment and ab initio calculations generally agree that the PO bond is strong, polar, and as short as conventional PO double bonds. The role of d functions as polarization functions rather than primary valence orbitals is well established.^{8,9} Where differences arise is in the interpretation of the bond based on different approaches.

Reed and Schleyer¹⁰ view the bonding as a donor–acceptor interaction with superimposed oxygen π orbital back-bonding with the degenerate H₃P moiety antibonding orbitals (negative hyperconjugation¹¹). Gordon and co-workers^{12–14} use energy-localized orbitals^{15–17} to picture the bond as one strong PO σ bond and three equivalent oxygen orbitals characterized primarily as lone pairs polarized toward phosphorus and staggered with respect to the PR bonds. At the same time, they¹² and others^{18,19} derive a

picture based on the Boys localization scheme^{20,21} that involves a single lone pair orbital on oxygen pointing away from the H₃P group in H₃PO and three bent or banana bonds strongly polarized toward oxygen. Reed and Schleyer¹⁰ employed natural localized molecular orbitals^{22,23} derived from a natural bond order analysis²⁴ to conclude that the bonding was dominated by ionic interactions and negative hyperconjugation. The fact that three quite different orbital schemes arise from basically the same Hartree–Fock (HF) density illustrates the arbitrary nature of this subdivision of charge.

The approximate generalized valence bond (GVB-SOPP) method also leads to three bent bonds between P and O in H₃-PO.²⁵ Although a set of unique orbitals is given by the valence bond approach, the full GVB and approximate GVB-SOPP can yield different bond descriptions.^{26,27} Bent bonds generally result rather than the σ – π picture when the more robust GVB approach is taken.²⁷

More recently ab initio nuclear magnetic resonance (NMR) calculations on the effect of correlation on phosphorus shielding in the phosphine oxides²⁸ clearly suggest the absence of conventional multiple bonding in the PO bond. Atoms-in-molecules^{29,30} (AIM) studies yield localized molecular orbitals^{31–33} that indicate one highly polarized σ bond plus strong back-bonding of the oxygen π orbitals. Although it has been argued that the strong character of the PO bond in the phosphine oxides is conveyed best by the R₃P=O formula, this latter study suggests that the situation is better pictured as R₃P⁺–O[–]. These results are in agreement with conclusions reached by Rai and Symons³⁴ and by Power³⁵ based on experimental ESR and NMR data, respectively.

A key question is the disposition of the oxygen lone pairs. Using Bader's AIM approach involving the Laplacian of the electron density, MacDougall and Hall³⁶ and more recently Dobado et al.³⁷ concluded the presence of three nonbonded maxima behind the oxygen atom (away from phosphorus) and staggered with respect to the R₃P bonds to indicate the lone pairs. They also conclude that the PO bond is highly ionic.

The electron localization function is a robust descriptor of chemical bonding based on topological analysis of local quantum mechanical functions related to the Pauli exclusion principle. It was first introduced by Becke and Edgecombe¹ and has been developed and applied extensively.^{2–5} The local maxima of the function define localization attractors corresponding to core, bonding (located between the core attractors of different atoms), and nonbonding electron pairs and their spatial arrangement.

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For a single determinantal wave function built from Hartree–Fock or Kohn–Sham orbitals φ_j

$$\text{ELF} = \frac{1}{1 + \left(\frac{D}{D_h}\right)^2} \quad (1)$$

where

$$D = \frac{1}{2} \sum_{j=1}^N |\nabla \varphi_j|^2 - \frac{1}{8} \frac{|\nabla \rho|^2}{\rho}$$

$$D_h = \frac{3}{10} (3\pi^2)^{2/3} \rho^{5/3}$$

$$\rho = \sum_{j=1}^N |\varphi_j|^2 \quad (2)$$

The localization function can be viewed as a local measure of the Pauli repulsion between electrons due to the exclusion principle and allows one to define regions of space that are associated with different electron pairs in a molecule or solid. It is large where the Pauli repulsion is small, that is, where two electrons with antiparallel spin are paired in space, and, conversely, it is small in the regions between electron pairs. The position where ELF attains a maximum value (the attractor) can be used as an electron pair's signature.

ELF values were obtained with the ToPMod program³⁸ at the B3LYP level^{39,40} using the 6-311(2df,2pd) basis⁴¹ for H_3PBH_3 , H_3PCH_2 , H_3PNH , and H_3PO employing structures optimized at the MP2(FC)/6-31+G(d,p) level of theory⁴¹ as implemented in the Gaussian 98 program.⁴² The ELF isosurfaces for H_3BH_3 , H_3PCH_2 , and H_3PNH (not shown) were obtained with the SciAn code⁴³ and display the expected nuclear attractors, the PB, PC, and PN bond attractors, and lone pair attractors. The staggered nature of the boron, carbon, and nitrogen protons and their lone pairs is observed, being precisely in those regions of space one would predict on simple chemical principles. The results for H_3PO are illustrated in the three parts of Figure 1 for the ELF = 0.796 (a), ELF = 0.800 (b), and (c) ELF = 0.825, isosurfaces. The figure focuses on the oxygen atom with the view toward oxygen being from somewhat to the right of the phosphorus atom (whose PH basins are not shown). Figure 1a displays the nearly spherical valence shell of the lone pairs surrounding the oxygen core and the small, triangular-shaped PO bond surface. Figure 1b shows how the PO bond surface is converging toward three maxima and how the lone pair surface is distorted toward these points. In Figure 1c the PO bond maxima have vanished and the oxygen valence shell is converging to three lone pair attractors staggered with respect to the PH bonds and on that side of oxygen opposite to the phosphorus atom. We believe the distortion of

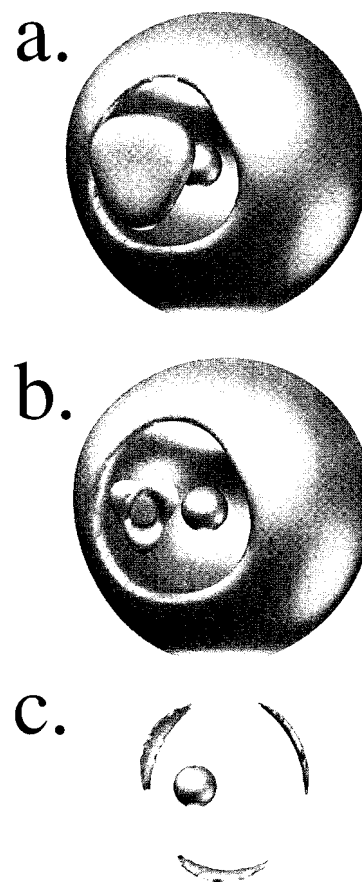


Figure 1. Isosurfaces around oxygen in H_3PO corresponding to ELF values of (a) 0.796, (b) 0.800, and (c) 0.825.

the lone pair shell in Figure 1a and b and the fact that the PO bond surface is converging to three maxima that are eclipsed to the lone pairs is consistent with the highly ionic nature of the PO bond and the polarized lone pairs back-bonding to phosphorus; Pauli repulsion between the lone pairs and separate bond attractors would be expected to lead to a staggered arrangement. The inconspicuous presence of the PO bond surface as a separate entity occurs over only a very small region of ELF values (approximately 0.01), also consistent with the highly ionic nature of the bond. Integrating the electron density over the attractor basins⁴⁴ yields electron counts of approximately two each for the PH bonds, the oxygen core, lone pairs, and PO bond and 10 for the phosphorus core. There is no indication of banana bonds. Rather, our results show the chemically expected staggered trigonal arrangement of electron lone pairs about oxygen to be the correct picture and are consistent with the lone pair polarization and back-bonding picture of stabilization of the PO bond in phosphine oxides.

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