Nature of the P–O bond in diphenylphosphonic acid: experimental charge density and electron localization function analysis

Konstantin A. Lyssenko,* Gennadii V. Grintselev-Knyazev and Mikhail Yu. Antipin

*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation.
Fax: +7 095 135 5085; e-mail: kostya@xrlab.ineos.ac.ru*

Analysis of the electron density function and the ELF on the basis of the high resolution diffraction X-ray investigation of $Ph_2P(O)OH$ at 110 K have revealed that, in the vicinity of the oxygen atom of the P=O group, three lone pairs in an antiperiplanar orientation in respect to OH and Ph substituents are localised.

Numerious quantum-chemical and experimental investigations of multiple bonds formed by transition elements have shown that the $3d$-orbital contribution to bonds of the above type is neglible.[1] These data led to a revision of some theoretical schemes, in particular, for the formally double P=O bond in phosphine oxides ($X_3P=O$).[1(d)]

A number of models were proposed for the description of the P–O bond in $X_3P=O$ compounds. In these models, the P–O bond is described as (*a*) one σ dative bond with additional backdonation of the oxygen's electron lone pair (Lp) to an appropriate antibonding orbital of the X_3P moiety [Figure 1(*a*)],[2] (*b*) one σ-bond of the exchange type (X_3P^+–O^-) with negative hyperconjugation between the π-type Lp orbitals of oxygen and antibonding σ bonds of the X–P bonds [Figure 1(*b*)],[1(b),(c)] or (*c*) three 'banana' bonds (Ω-bonds)[3] [Figure 1(*c*)]. It should be noted that these different models were obtained using the same level of theory applying different methods of orbital localization.[1(d),4]
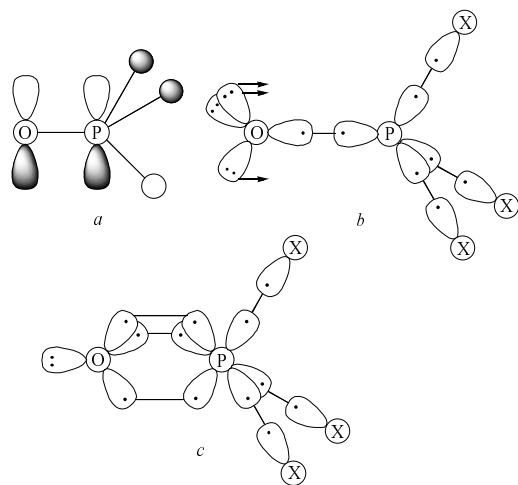
Figure 1 Models (*a*)–(*c*) proposed for the description of the P–O bonding in phosphine oxides.

Depending on the model (*a*)–(*c*), the number and mutual positions of the lone pairs localised at the oxygen atom appear differently. Therefore, the use of methods that allow one to localise the Lp, in particular such as topological analysis of the electron density function $\rho(r)$ and analysis of the electron localization function (ELF), seems to be the most appropriate way to investigate the P–O chemical bonding pattern.

Theoretical topological analysis of the $\rho(r)$[7] and of ELF[8] functions in $X_3P=O$ (X = H, Me) molecules has revealed that in the vicinity of the oxygen atom there are three electron lone pairs in an antiperiplanar conformation with respect to P–X bonds, which is in agreement with model *b*. However, these investigations did not provide data on the contribution of the $Lp_O \rightarrow \sigma^*(P-X)$-orbital back donation.

To estimate the correctness of model *b* (proposed for phosphine oxides) for compounds with different substituents at the phosphorus atom and to analyse the role of the back donation, we performed an analysis of the $\rho(r)$ function on the basis of
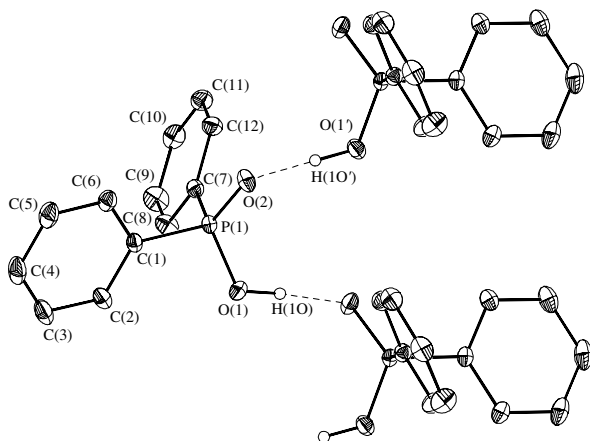
high-resolution X-ray diffraction data for diphenylphosphonic acid **1** at 110 K.[†] In addition, an analysis of the ELF obtained through recently proposed semiempirical representation of the kinetic energy density[13,‡] has been carried out.

According to model *b*, in the isolated $Ph_2(HO)PO$ molecule, the Lp → σ* interaction will lead to two types of lone pairs, one is antiperiplanar to the OH bond and the other (two Lp), to the phenyl group. However, in the crystal, the equivalence of two

---

The analytical form of electron density was obtained by a multipole refinement based on the Hansen–Coppens[9] formalism using the XD program[10] package. The level of the multipole expansion was octopole for all nonhydrogen atoms or dipole for hydrogens. The H(1O) atom, which forms the intermolecular H-bond, was refined up to a quadrupole level. The scattering factor of the hydrogen atoms was calculated from the contracted radial density functions (κ = 1.2). The rigid-bond test (Hirshfeld[11]) on anisotropic displacement parameters has shown that the difference between mean-square vibration amplitudes along the chemical bonds in **1** did not exceed 0.0007 Å^2. The refinement was carried out against F, the multipole occupancies of the carbon atoms of Ph rings were refined with the *m* symmetry restraints according to ref. 12. The refinement converged to R = 0.0306, wR = 0.0312, GOF = 1.152 for 6523 reflections with $I > 3\sigma(I)$. The ratio of the number of reflections to the number of refined parameters was greater than 18. Analysis of the deformation electron density, topology of the $\rho(r)$ function and of ELF was carried out using the WINXPRO 1.1 program package.[13]

Figure 2 General view of molecule **1** and the formation of the H-bond chains directed along the crystallographic axis *b*. The important bond lengths (Å): P(1)–O(1) 1.5498(6), P(1)–O(2) 1.5015(5), P(1)–C(1) 1.7908(6), P(1)–C(7) 1.7981(6); bond angles (°): O(2)–P(1)–O(1) 116.63(3), O(2)–P(1)–C(1) 110.38(3), O(1)–P(1)–C(1) 102.88(3), O(2)–P(1)–C(7) 111.00(3), O(1)–P(1)–C(7) 107.25(3), C(1)–P(1)–C(7) 108.14(3). The parameters of the intermolecular H-bond: O(1)–H(1O)···O(2′) (−*x*, 1/2 + *y*, 1/2 − *z*): O(1)···O(2′) 2.4792(8) Å, H(1O)···O(2′) 1.73(2) Å, O(1)H(1)O(2′) 172°.

lone pairs antiperiplanar to a phenyl group may be violated due to formation of H-bonds. Analysis of intermolecular contacts in **1** has revealed that the O(2) atom participates in a strong intermolecular H-bond with the P–OH group. This interaction is characterised by a short O···O distance of 2.4792(8) Å and a torsion angle H(1O′)O(2)P(1)C(1) of 174.1° and, therefore, may lead to inequivalence of the $\mathrm{Lp_{O(2)}} \to \sigma^*$ interaction for P(1)–C(1) and P(1)–C(7) bonds (Figure 2). Consequently, this difference might cause the shortening of the P(1)–C(1) bond relative to the P(1)–C(7) bond. While the geometry analysis of **1** has revealed such a shortening, it appeared to be too small [0.0073(6) Å], which makes only geometrical criteria to be insufficient to clarify the role of Lp → σ* interaction.

Analysis of the deformation electron density (DED) in the CP(1)O(2) and O(1)P(1)O(2) sections allows one to localise unambiguously only one Lp [which is antiperiplanar to the P–C(1) bond] involved in H-bonding [Figure 3(*a*)]. The DED distribution in the H-bond region is typical of the short O–H···O interactions, which is reflected, in particular, in the polarization of the O(2) atom Lp to the direction of the H(1O′) atom.

Analysis of critical points (CP) (3, −1) of the $\rho(r)$ function in **1** has revealed that the topological parameters of the P(1)–C(1) and P(1)–C(7) bonds are significantly different in spite of the proximity of their bond lengths. Thus, the values of $\rho(r)$ and $\nabla^2\rho(r)$ in the CP (3, −1) of the P(1)–C(1) bond (1.40 eÅ⁻³, −11.46 eÅ⁻⁵) are significantly larger at absolute scale than corresponding values for the formally equivalent P(1)–C(7) bond (1.22 eÅ⁻³, −8.48 eÅ⁻⁵). Taking into account that the value of $\rho(r)$ in CP (3, −1) correlates with the bond order,[5] the observed difference directly shows that the P(1)–C(1) bond is somewhat weaker than P(1)–C(7). It is intriguing that the decrease of

the P(1)–C(7) bond order is accompanied by an increase in its ellipticity (0.12) in comparison to the ellipticity of the P(1)–C(1) bond (0.08). Note that, in accordance with model *b*, these topological parameters are in agreement with the population scheme of the σ*[P(1)–C(7)] orbital due to the $\mathrm{Lp_{O(2)}} \to \sigma^*[P(1)–C(7)]$ interaction and the weakening of the $\mathrm{Lp_{O(2)}} \to \sigma^*[P(1)–C(1)]$ interaction due to participation of the corresponding Lp in H-bonding.

To estimate the O(2)···H(1O′)O(1′) H-bond strength, we carried out analysis of the topological parametrs of $\rho(r)$ in corresponding CP (3, −1). The relatively high value of $\rho(r)$ (0.45 eÅ⁻³) in CP (3, −1), in spite of a positive value of $\nabla^2\rho(r)$ (7.37 eÅ⁻⁵), indicates that the above H-bond corresponds to an intermediate rather than the closed-shell type of the interatomic interactions.[5,16]

This is supported by the fact that the local electron density [$E^e(r)$] in CP (3, −1) in the O(2)···H(1O′) interatomic area and estimated on the basis of the semiempirical representation of the $t(r)$[14,‡] is negative (−0.006 a.u.).[5]

The high strength of the H-bond in **1** also follows from the analysis of ELF function. It is can be seen in the map of the ELF in the O(1)P(1)C(1) plane [Figure 3(*b*)] that the formation of the H-bond leads not only to polarization of the Lp of the O(2) atom but also to deformation of the valence shell of the H(1O′) atom. The latter results in a decrease of ELF along the O···H vector. Such a redistribution of the electron density is characteristic of strong H-bonds[17] and, according to ref. 15, can be explained in terms of a key–lock mechanism which was proposed for strong secondary interactions such as Cl···Cl.[5] The other interesting feature of the ELF map is the presence of an additional maximum in the vicinity of the O(2) atom, which also corresponds to the oxygen Lp.

It was shown that H-bonds with an intermediate type of interatomic interactions are characterised by a low barrier of the hydrogen transfer and a high energy.[16] In fact, the energy of the H-bond (E_{HB}) estimated on the basis of correlation between the E_{HB} and $t(r)$[16,17] in **1** is equal to 25.8 kcal mol⁻¹. Therefore, the presence of the strong O(2)···(1O′)O(1′) bond can reduce or even completely exclude the contribution of the $\mathrm{Lp_{O(2)}} \to \sigma^*[P(1)–C(1)]$ interaction to P(1)–O(2) chemical bonding.

While the experimental data on the electron density function are in agreement with the presence of back donation from the O(2) atom Lp to antibonding orbitals of C₂OP fragment (model *b*), they also partly agree with model *a*, in which similar charge transfer can occur (Figure 1).

Taking into account that the possible remaining lone pairs of the O(2) atom in model *a* or *b* will be 'indrawn' in the area of the valence electrons concentration of the oxygen atom, a further analysis of the DED and ELF has been carried out in the sections parallel to the plane of O(1), C(1) and C(7) atoms and 0.1–0.2 Å above the O(2) atom. The choice of this range of distances was based on the results of a theoretical topological analysis of the $\rho(r)$ function in Me₃PO, according to which the maxima corresponding to the lone pairs are localised at distances up to 0.30 Å from the atomic nuclei.[7]

In the DED section drawn above 0.20 Å from the O(1) atom [Figure 4(*a*)], an additional maximum antiperiplanar to the C(7)
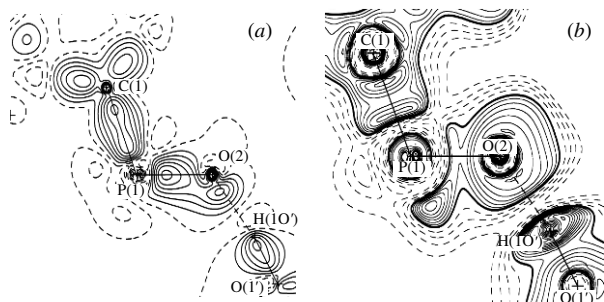
Figure 3 (*a*) DED and (*b*) ELF distributions in the C(1)P(1)O(2) plane of **1**. Contours are drawn with 0.1 step. The negative contours of DED (*a*) and the values of ELF < 0.5 (*b*) are dashed. The contour of ELF equal to 0.5 is drawn by a thicker line.
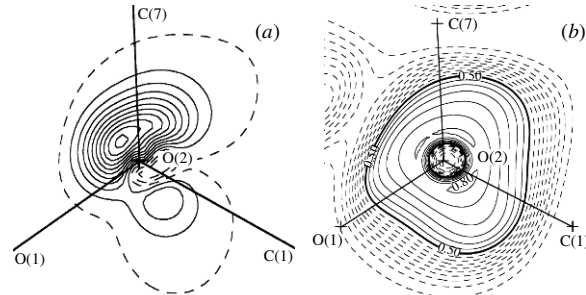
Figure 4 (*a*) DED and (*b*) ELF distributions in the section parallel to the plane of O(1), C(1) and C(7) atoms at a distance 0.2 Å from the O(2) atom. The negative contours of DED (*a*) and values of ELF < 0.5 (*b*) are dashed. The contour of ELF equal to 0.5 is drawn by a thicker line.

atom in addition to Lp involved in an H-bond was revealed. It should be noted that the observed DED distribution (due to the diffuse character of Lp) is susceptible with the presence of a third maximum antiperiplanar to the P(1)–O(1) bond. In the case of ELF, which is a more accurate method for the localization of lone pairs,[6] analysis of the above section makes it possible to localise three maxima oriented in the staggered orientation with respect to the C(1)C(7)O(1) fragment [Figure 4(*b*)]. Note that maxima of ELF (0.80) corresponding to the possible positions of lone pairs in **1** are in very good agreement with corresponding quantum-chemical data for ELF (0.825) in Me_3PO.[8]

Thus, topological analysis of electron density and ELF distributions obtained on the basis of the X-ray investigation in diphenylphosphinic acid [$Ph_2P(O)OH$] demonstrated that the most correct model for the description of the PO chemical bond in this compound is model *b*, as it was found earlier in phosphine oxides (X_3PO), where three lone pairs were localised at the oxygen atom.[1(b)] At the same time, in contrast to theoretical investigations, the presence of the strong O–H···O interaction makes it possible to confirm the contribution of the $Lp_O \rightarrow \sigma^*(P–X)$ back donation in P–O bonding.

References

1 (*a*) E. Magnusson, *J. Am. Chem. Soc.*, 1990, **112**, 7940; (*b*) A. Streitwieser, A. Rajca, R. S. McDowell and R. Glaser, *J. Am. Chem. Soc.*, 1987, **109**, 4184; (*c*) A. Streitwieser, R. S. McDowell and R. Glaser, *J. Comput. Chem.*, 1987, **8**, 788; (*d*) D. G. Gilheany, *Chem. Rev.*, 1994, **94**, 1339.

2 (*a*) M. S. Gordon, J. A. Boatz and M. W. Schmidt, *J. Phys. Chem.*, 1984, **88**, 2998 (*b*) M. W. Schmidt and M. S. Gordon, *J. Am. Chem. Soc.*, 1985, **107**, 1922.

3 (*a*) R. P. Messmer, *J. Am. Chem. Soc.*, 1991, **113**, 433; (*b*) C. H. Patterson and R. P. Messmer, *J. Am. Chem. Soc.*, 1989, **111**, 8059; (*c*) C. H. Patterson and R. P. Messmer, *J. Am. Chem. Soc.*, 1990, **112**, 4138.

4 M. W. Schmidt, S. Yabsuhita and M. S. Gordon, *J. Phys. Chem.*, 1984, **88**, 382.

5 (*a*) R. F. W. Bader, *Atoms in molecules. A quantum theory*, Clarendron Press, Oxford, 1990; (*b*) R. F. W. Bader, *J. Chem. Phys.*, 1998, **A102**, 7314; (*c*) R. F. W. Bader and H. Essen, *J. Chem. Phys.*, 1984, **80**, 1943; (*d*) R. F. W. Bader, S. Johnson, T.-H. Tang and P. L. A. Popelier, *J. Phys. Chem.*, 1996, **100**, 15398.

6 A. Savin, R. Nesper, S. Wengert and T. Fassler, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1808.

7 J. A. Dobado, H. Martinez-Garcia, J. M. Molina and M. R. Sundberg, *J. Am. Chem. Soc.*, 1998, **120**, 8461.

8 D. B. Chesnut and A. Savin, *J. Am. Chem. Soc.*, 1999, **121**, 2335.

9 N. K. Hansen and P. Coppens, *Acta Crystallogr.*, 1978, **A34**, 909.

10 T. Koritsansky, S. T. Howard, T. Richter, P. R. Mallinson, Z. Su and N. K. Hansen, *XD, a Computer Program Package for Multipole Refinement and Analysis of Charge Densities from X-ray Diffraction Data*, 1995.

11 F. L. Hirshfeld, *Acta Crystallogr.*, 1976, **A32**, 239.

12 K. Kurki-Suonio, *Israel J. Chem.*, 1977, **16**, 115.

13 (*a*) A. Stash and V. Tsirelson, *WinXPRO, a Program for Calculation of the Crystal and Molecular Properties Using the Model Electron Density*, 2001. A further information available at http://xray.nifhi.ru/wxp/; (*b*) A. Stash and V. Tsirelson, *J. Appl. Crystallogr.*, 2002, **35**, 371.

14 D. A. Kirzhnits, *Sov. Phys. JETP.*, 1957, **5**, 64.

15 V. Tsirelson and A. Stash, *Chem. Phys. Lett.*, 2002, **351**, 142.

16 K. A. Lyssenko and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 400 (*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 418).

17 E. Espinosa, E. Mollins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170.

18 F. Fuster and B. Silvi, *Theor. Chem. Acc.*, 2000, **104**, 13.