Electron Density Distribution in Diphosphenes and the Nature of the Phosphorus−Phosphorus Double Bond: Experimental and Theoretical Studies

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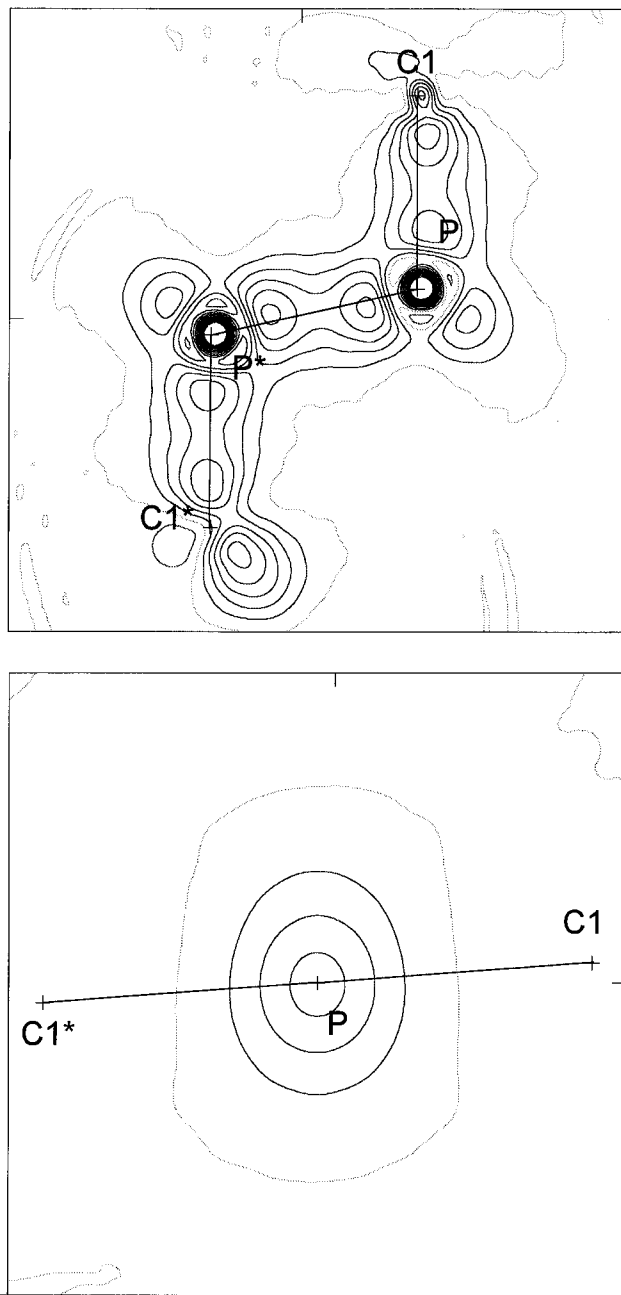Tom Ziegler[||]

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One of the exciting developments in main group chemistry in recent years has been the isolation of compounds that feature double bonding between the heavier group 14 or 15 elements.[1] However, despite the rapid progress that has been made in this area since the early 1980s, there have been no experimental studies of the electron distributions in diphosphenes (RP=PR), disilenes ($R_2Si=SiR_2$), or their heavier congeners. Experimental electron deformation density (EDD) determination is a technique that is capable of furnishing unique and useful insights into chemical bonding,[2] and herein, we describe the first such study of a diphosphene. As a check of the validity of the conclusions from the EDD data, we have also conducted a companion theoretical study using density functional theory (DFT).[3] The latter approach has been applied succesfully to the analysis of double bonds involving the group 14 elements.[4]

The X-ray crystal structure of $(2,4,6,-t\text{-}Bu_3C_6H_2)P=P(2,4,6,-t\text{-}Bu_3C_6H_2)$ (**1**)[5] has been reported previously; however, for the present purpose, it was necessary to acquire high-precision, high-angle ($\sin \theta/\lambda)_{max} = 0.90$; $2\theta_{max} = 80°$) X-ray data at low temperature (100 K).[6]

Molecules of **1** reside on a crystallographic inversion center. The EDD plots shown in Figure 1 were obtained by a multipole refinement in which no constraints were employed for the

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　(1) For reviews, see: (a) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (b) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (c) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1. (d) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386. (e) Weber, L. *Chem. Rev.* **1992**, *92*, 1839. (f) Norman, N. C. *Polyhedron* **1993**, *12*, 2431.
　(2) (a) Coppens, P. Experimental Electron Density. In *Annual Review of Physical Chemistry*; Strauss, H. L., Babcock, G. T., Leone, S. R., Eds.; Annual Reviews Inc.: Palo Alto, CA, 1992; p 663. (b) Angermund, K.; Claus, K. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 237. (c) Antipin, M. Y.; Chernega, A. N.; Lysenko, K. A.; Struchkov, Y. T.; Nixon, J. F. *J. Chem. Soc., Chem. Commun.* **1995**, 505.
　(3) Ziegler, T. *Pure Appl. Chem.* **1991**, *28*, 1271. Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. *Density Functional Methods in Chemistry*; Labanowski, J., Andzelm, J., Eds.; Springer-Verlag: Heidelberg, 1991.
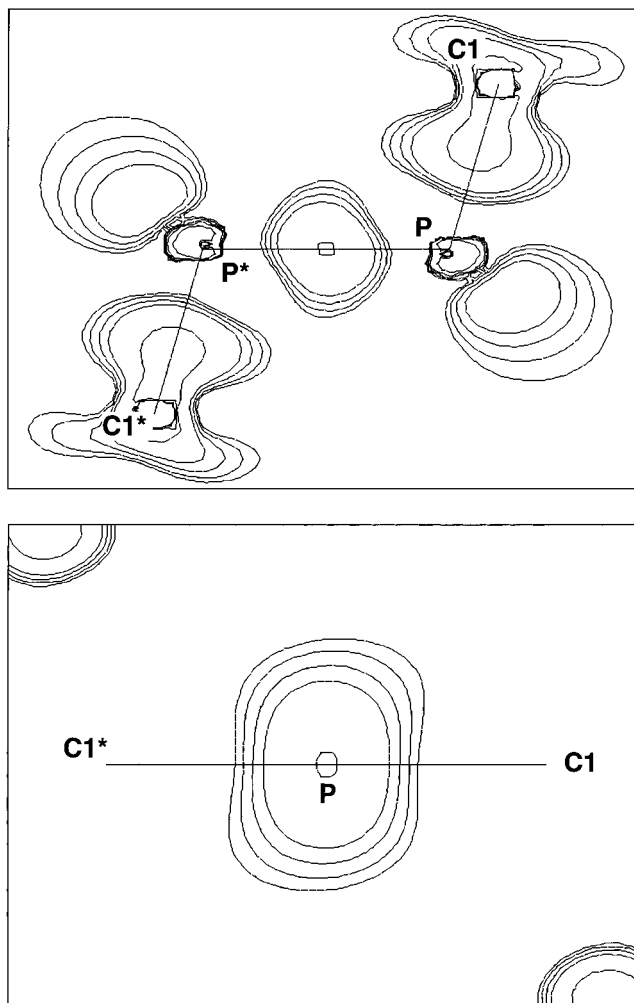　(4) Jacobsen, H.; Ziegler, T. *J. Am. Chem. Soc.* **1994**, *116*, 3667.
　(5) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, K. *J. Am. Chem. Soc.* **1981**, *103*, 4587.
　(6) X-ray data for **1**: $C_{36}H_{58}P_2$, $M_r = 552.8$, monoclinic, $C2/c$, $a = 16.774(4)$ Å, $b = 9.825(3)$ Å, and $c = 20.578(2)$ Å, $\beta = 98.830(9)°$, $V = 3351.2$ Å^3, $Z = 4$, $D_c = 1.096$ g cm^{-3}, $\mu = 1.47$ cm^{-1}, λ(Mo Kα) = 0.71069 Å, $T = 100$ K. On an Enraf Nonius CAD 4 diffractometer were collected 35 975 reflections ($1° \leq \theta \leq 40°$) of which 4428 independent reflections ($I > 2\sigma(I)$) were used for full-matrix least-squares refinement: final $R = 0.026$, $R_w = 0.029$. The full data set was used for the multipole expansion. Atomic coordinates, thermal parameters, and scale factors were taken from the high-order refinement data; for phosphorus and carbon, the multipole coefficients were developed to the octopole level. The program MOLLY (Hansen, N. K.; Université de Nancy, I, France, 1981) was used for the multipole refinement.

Figure 1. (a) EDD map for the C−P−P−C plane of **1**. Solid and dotted lines indicate positive and negative values of EDD, respectively. The contours are drawn at intervals of 0.1 e/Å^3. (b) EDD map at the midpoint of the P−P vector in **1** in the plane perpendicular to the C−P−P−C plane. Solid and dotted lines indicate positive and negative values of EDD, respectively. The contours are drawn at intervals of 0.1 e/Å^3.

phosphorus atoms but local *mm*2 and 3*m* symmetries were assumed for the aryl-C and *t*-Bu groups, respectively.[6,7] Figure 1a illustrates the EDD in the C−P−P−C plane. Highly positive EDD values are evident on the phosphorus atoms in a region corresponding to that anticipated for lone pairs.[8] Figure 1b shows the EDD at the midpoint of the P−P vector in the plane perpendicular to the C−P−P−C plane. The distribution is distinctly noncylindrical. A cut through a pure σ-bond would

　(7) Lutz, F. Ph.D. Dissertation, Universität Wuppertal, Germany, 1993.
　(8) The double peaks in the P=P and P−C regions of the experimental density are associated with a biased structure model caused by the use of spherical atoms. This is a well-known feature of EDD maps involving heavier atoms. For example, see: Wang, Y.; Coppens, P. *Inorg. Chem.* **1976**, *15*, 1122. Coppens, P.; Yang, Y. W.; Blessing, R. H.; Cooper, W. F.; Larsen, F. K. *J. Am. Chem. Soc.* **1977**, *99*, 760. See also, ref 7.

give rise to circular contours, and the observation that the EDD is elongated in the direction anticipated for the π-bond is consistent with a double bond description.[9] Preliminary experiments[7] reveal similar EDD contours for $(Me_3Si)_3CP{=}PC{-}(SiMe_3)_3$ (**2**).[10]

With a view toward gaining a more detailed understanding of the P=P bond and allowing the best comparison with the EDD results, we chose to perform DFT calculations on the actual diphosphene **1**.[11] Previous calculations have been devoted to the simplified model diphosphene HP=PH.[12] The DFT calculations indicate that HOMO of **1** is 60% P based, with contributions of 54% p_x, 32% p_y, and 14% s, respectively. This orbital corresponds to the phosphorus lone pairs, which are therefore mainly of p-type character. The HOMO-1 is 50% based on the heavy atoms, which contribute almost exclusively with their p_z orbitals, and represents the π_{pp}-bond. The HOMO and the HOMO-1 are very close in energy, being separated only by 0.324 eV. The Hirshfeld analysis[13] assigns a charge of +0.163 to the P centers, thus indicating a small amount of electron donation from the heavy elements into the aromatic rings. DFT calculations have also been performed on $\{2,4,6\text{-}(CF_3)_3\text{-}C_6H_2\}P{=}P\{2,4,6\text{-}(CF_3)_3C_6H_2\}$ (**3**), based on the X-ray derived structure,[14] and reveal a similar ordering of orbital energies. We note that the nature of the HOMO and HOMO-1 was one of the questions raised in earlier theoretical studies of the parent diphosphene, *trans*-HP=PH. The results of SCF calculations[12] revealed the π_{pp}-orbital to be the HOMO and the phosphorus-based lone pairs orbital to be the HOMO-1. In more accurate CI calculations,[12] the sequence of these two orbitals is inverted in accord with the present DFT results.

The calculated deformation density (CDD) of **1** was obtained by subtraction of the superposition of the atomic fragment densities from the final density of the molecule. Two representative plots are shown in Figure 2. Figure 2a shows the CDD in the C$-$P$-$P$-$C plane. The build up of density corresponding to the free lone pairs of the P atoms is clearly apparent and is in satisfactory agreement with the experimental EDD (Figure 1a). The lone pairs are centered about 0.75 Å away from the P atoms. The CDD in the plane perpendicular to the C$-$P$-$P$-$C plane at the midpoint of the P$-$P vector is shown in Figure 2b. The build up of density corresponds to the P$-$P σ- as well

(9) Gillespie, R. J.; Robinson, E. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 495. Buschmann, J.; Koritsanszky, T.; Kuschel, R.; Luger, P.; Seppelt, K. *J. Am. Chem. Soc.* **1991**, *113*, 233.

(10) Cowley, A. H.; Kilduff, J. E.; Norman, N. C.; Pakulski, M.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4845.

(11) The DFT calculations utilized the ADF program package (Baerends, E. J.; Ellis, D. E.; Ros, P. E. *Chem. Phys.* **1973**, *2*, 41; teVelde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84), release 2.0.1. Nonlocal gradient corrections due to exchange (Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 1053) and correlation (Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822) were included self-consistently. Use was made of the frozen core approximation and density fit. The valence shells of the atoms were described by a double-ζ STO basis set, augmented by one 3d polarization function for C and P and by one 2p polarization function for H (ADF basis set III). The numerical integration grid was chosen in such a way that significant test integrals were evaluated with an accuracy of at least four significant digits. For a more detailed description, as well as further references, see: teVelde, G. *ADF 2.0.1 User's Guide, Scientific Computing and Modelling*; Amsterdam, The Netherlands, 1995.

(12) For example, see: Allan, T. L.; Scheiner, A. C.; Yamaguchi, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 7579.

(13) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129.

(14) Cowley, A. H., Decken, A., Isom, H. S., unpublished results. For the synthesis of this compound, see: Scholz, M.; Roesky, H. W.; Stalke, D.; Keller, K.; Edelmann, F. T. *J. Organomet. Chem.* **1989**, *366*, 73.

Figure 2. (a) CDD map for the C$-$P$-$P$-$C plane of **1**. Only positive values of CDD are shown. The contour values are 0.001, 0.003, 0.006, 0.01, and 0.03 e/(au)^3. (b) CDD at the midpoint of the P$-$P vector in the plane perpendicular to the C$-$P$-$P$-$C plane. Other details are as indicated in Figure 2a.

as π-bonds and again agrees extremely well with the experimental contours (Figure 1b).

In conclusion, it has been found that experimental electron deformation densities agree very favorably with those obtained by DFT calculations. Furthermore, the DFT calculations reveal that the HOMO of the P=P compounds corresponds to the two phosphorus lone pairs, while the HOMO-1 comprises the phosphorus$-$phosphorus π-bond. Further studies on diimines and diarsenes are in progress in order to study group trends.

Supporting Information Available: X-ray structural data for **1** including a summary of crystallographic parameters, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles (7 pages). See any current masthead page for ordering and Internet access instructions.

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