

Electron Distribution in *tert*-Butyl Phosphaethyne Bu^tC≡P

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The first high-precision, low-temperature, X-ray diffraction study on a phosphaalkyne reveals that the lone pair electrons are located much closer to the P atom than in the related phosphaalkene, and furthermore there is a significant excess electron density on the sp-hybridised C atom, thus readily accounting for the remarkable preferential protonation at C rather than at P in spite of the presence of the lone-pair electrons.

One of the most exciting recent developments in organo-phosphorus chemistry has been the synthesis and characterisation of compounds that contain multiple phosphorus–element bonds.¹ The existence of these compounds showed that the so-called ‘double-bond rule’, according to which thermally stable compounds containing multiple bonds would occur only for elements of the second period, must be overthrown. Thus, it is not surprising that details of the molecular and electronic structure of phosphaalkynes, RC≡P, are of considerable interest both for organoelement and theoretical chemistry and they have been the subject of an increasing number of studies by X-ray,² microwave,³ photoelectron⁴ and quantum-chemical⁵ methods.

In recent years, electron-density distribution (EDD) maps, obtained as a result of high-precision low-temperature X-ray diffraction studies of single crystals, have been widely used in interpreting chemical bonding in both organic and organo-element compounds.⁶ We have previously studied certain two-coordinated phosphorus derivatives⁷ and now present the first experimental EDD study of a monocoordinated phosphorus compound, namely the phosphaalkyne, Bu^tC≡P **1**. The general view of the molecule **1** and its relevant geometrical parameters are given in Fig. 1, and the experimental deformation electron density (DED) map in the section through the P, C(1), and C(2) atoms and normal to the crystallographic and molecular plane is shown in Fig. 2.

The molecular geometry of **1** is unexceptional and the very short P≡C triple bond length 1.548(1) Å is quite close to the experimental microwave data for HC≡P (1.5404 Å,^{3d}), MeC≡P [1.544(4) Å,^{3e}], and Bu^tC≡P (1.536 Å,^{3c}). It should be noted that at high-order refinement, this bond is insignificantly elongated only to 1.550(1) Å.

The most noteworthy features of the DED map of **1** are associated with the regions of the phosphorus lone pair LP(P) and the P≡C triple bond. The peak A with a height of 0.41 e Å⁻³ corresponding to the LP(P) is situated at 0.55 Å from the P atom nucleus along the extension of the C(1)–P line. In the

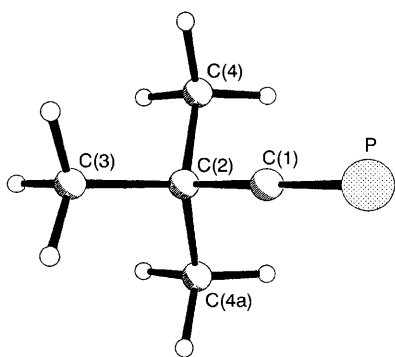


Fig. 1 The general view of the molecule **1** and atomic numbering. Bond lengths and angles: P–C(1) 1.548(1), C(1)–C(2) 1.473(1), C(2)–C(3) 1.540(1), C(2)–C(4) 1.539(1) Å; P–(C1)–C(2) 179.5(1), C(1)–C(2)–C(3) 109.6(1), C(1)–C(2)–C(4) 109.3(1), C(4)–C(2)–C(4a) 109.8(1), C(3)–C(2)–C(4) 109.4(1)°.

corresponding DED map calculated with the inclusion of all reflections the height of this peak increases only to 0.46 e Å⁻³. It is interesting to note that this peak is located much closer to the phosphorus nucleus than was found for the respective peaks in the phosphaalkenes R₂C=PX, (0.65–0.85 Å)^{7a,b} [X = H, N(SiMe₃)₂]. This decrease of the P···LP(P) distance is most readily attributable to the different character of the P atom hybridization in phosphaalkynes (sp) and in phosphaalkenes (sp²).

The DED peak of the triple P≡C bond has a pronounced saddle-like shape, containing two local maxima with heights of 0.37 e Å⁻³ at a distance of 0.34 Å from the P atom and 0.26 e Å⁻³ at 0.45 Å from the C(1) atom, and a saddle point of 0.19 e Å⁻³ almost in the middle of the P···C(1) line. This feature of the DED in the P≡C triple bond differs considerably from that found in the N≡C triple bond of the cyano group in tetracyanoethyleneoxide,⁸ which was only one peak elongated in the directions orthogonal to the N···C line and whose maximum is shifted along this line towards the carbon atom.

It is also noteworthy that the peak of 0.45 e Å⁻³ for the single C(1)–C(2) bond in **1** is shifted by 0.35 Å from the midpoint towards the C(1) atom indicating significant polarity of this bond. This result is in a good agreement with the *ab initio* quantum-chemical calculation of the model molecule MeC≡P,^{5b} which shows a significant excess electron density on the C(1) (sp) atom in comparison to that of the C(2) (sp³) atom.

A multipole refinement of the structure of **1** was also performed using an LSMOL program and the Hansen–Coppens approach for the multipole EDD representation of the aspherical atom.⁹ The atomic charges of the P, C(1) and C(2) atoms derived from the kappa-refinement were found to be +0.22(3) and –0.43(3), respectively, which are in qualitative agreement with the corresponding values for this molecule calculated by us

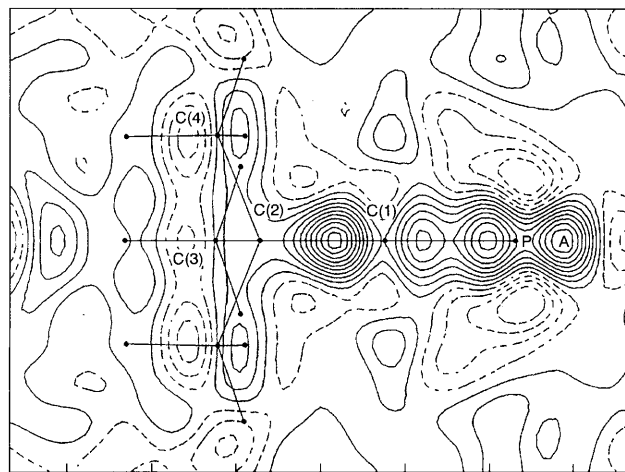


Fig. 2 Deformation electron density map in the molecule **1** through P, C(1), C(2) atoms in the section normal to the molecular and crystallographic plane. Negative contours dashed, isolines are drawn at 0.05 e Å⁻³.

using *ab initio* RHF/3-21G* (+0.124 and -0.114) and RHF/6-31G* (+0.025 and -0.118) methods with the molecular geometry optimization. It should be noted for comparison, that an *ab initio* SCF calculation of the related molecule MeCP gives charges for P and C(sp) atoms as +0.23 and -0.43, respectively,^{5b} that are very close to those obtained from the multipole model. The dipole moment of the phosphalkyne **1**, calculated from the multipole data was found to be 1.70 D, which is a little larger than that determined experimentally for the same compound (1.24 D).¹⁰ It has been reported previously¹¹ that the multipole model usually results in higher values for the dipole moments of organic molecules in crystals. On the other hand, the quantum-chemically calculated dipole moment of **1** in RHF/3-21G* and RHF/6-31G* approximations (1.66 and 1.82 D respectively) is much closer to the multipole value. The calculated P-C(1) and C(1)-C(2) bond lengths (1.519/1.523 and 1.471/1.480 Å, respectively, for the two calculations), are very similar to the experimental diffraction data [1.548(1) and 1.473(1) Å].

The results of the multiple EDD study on **1** which confirm the positive charge on phosphorus and the negative charge at C(1) has very interesting chemical consequences, and readily accounts for the remarkable recent results of Regitz and coworkers¹² who have shown that protonation of **1** at low temperature occurs exclusively at the C(1) centre rather than at the phosphorus lone pair.

We thank the Ukrainian State Committee for Science and Technology, the International Science Foundation (Grant M1F000) and the SERC for financial support.

Received, 2nd November 1994; Com. 4106703G

Footnote

† Crystal data for: **1**: C₅H₉P, *M* = 100.1, orthorhombic, space group *Cmc*2₁ (*C*_{2v}¹²), at 125 K: *a* = 8.868(1), *b* = 7.079(1), *c* = 10.656(2) Å, *V* = 655.2(3) Å³, *Z* = 4 (molecule has crystallographic *m*-plane), *D*_c = 1.015 g cm⁻³, *μ* = 2.9 cm⁻¹, *F*(000) = 216, diffractometer 'Siemens P3/PC', Mo-Kα radiation, graphite monochromator, *θ*/*2θ*-scan method, *2θ* ≤ 100°, 7335 measured reflections (the full sphere of the reciprocal space in the interval *2θ* ≤ 65° and half-sphere in the interval 65° < *2θ* ≤ 100°), *R*_{int} = 0.029 for all reflection and 0.012 for low-angle reflection with *2θ* ≤ 65°, 2596 unique observable reflections with *I* ≥ 2σ(*I*).

Compound **1** is a liquid at room temperature, and a single crystal suitable for X-ray diffraction study was grown in a thin-walled capillary (diameter ca. 0.4 mm) by very slow cooling of its melt near the melting point ca. 193 K. The single crystal so obtained was slowly cooled further to 125 K and the X-ray diffraction experiment was carried out at this temperature. The structure was solved and refined to *R* = 0.0264, *R*_w = 0.0320 and GOF = 1.27 using the SHELXTL PLUS program package on a IBM/PC-computer using 1833 independent reflections with *I* ≥ 4σ(*I*) in the full-matrix anisotropic (C,P-atoms)—isotropic (H-atoms) approximation with the isotropic extinction correction.

DED maps were obtained with a conventional 'X-X' method using a high-order refined atomic model (sin *θ*/*λ* > 0.65 Å⁻¹, 1067 reflections with *I* ≥ 4σ(*I*), *R* = 0.030, *R*_w = 0.032, GOF = 1.02, H-atoms were fixed at ideal positions with the isotropic *U*-values) and low-angle diffraction data (sin *θ*/*λ* ≤ 0.70 Å⁻¹). The corresponding DED map with the inclusion of all reflections does not essentially differ from the map shown. The multipole population parameters of the C and P atoms were refined up to octopole level (*l* = 3) and dipole level (*l* = 2) for H-atoms together with the positional and thermal atomic parameters using all reflections. The final *R*-values were equal to *R* = 0.0177, *R*_w = 0.0161, GOF = 1.14.

Bond lengths and angles, atomic coordinates, and thermal parameters are deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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