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# Molecular and Crystal Structure of *Tert*-Butylphosphaethyne

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## ABSTRACT

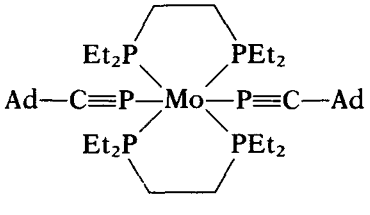
*The crystal and molecular structure of* tert-*butylphosphaethyne, $Bu^tC{\equiv}P$, liquid at room temperature, has been determined by X-ray diffraction at 108 K. Main geometrical parameters are as follows: P≡C 1.542(2), C(sp)–C($sp^3$) 1.470(3) Å, PCC 179.3(2)°.*

## INTRODUCTION

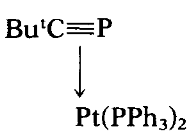
In comparison with other types of organophosphorus compounds the geometry of phosphaalkynes RC≡P has been studied much less extensively. Thus the Cambridge Database file [1] contains the X-ray structure of only one representative of this class, namely, 2,4,6-tri(*tert*-butyl)phenylphosphaethyne, ($C_6H_2Bu^t_3$)C≡P, (**1**) [2]. Microwave studies are somewhat more numerous [3], however this method in many cases involves a number of geometrical assumptions or restrictions. At the same time the peculiarities of the phosphaalkyne molecular geometry represent considerable interest both for organoelement and theoretical chemistry. In this connection we have therefore carried out the low temperature X-ray structural investigation of *tert*-butylphosphaethyne, $Bu^tC{\equiv}P$ (**2**), which is a liquid at room temperature, and has been the most widely studied of the phosphaalkynes [4].

## DISCUSSION

The general view of the $Bu^tC{\equiv}P$ molecule is shown in Figures 1 and 2. The triple P≡C bond length 1.542(2) Å in (2) is equal within the experimental error to the corresponding parameters 1.516(13) and 1.520(12) Å observed in molecule (**1**) [2] and the *bis*-$\eta^1$-complex (**3**), respectively [5].



**3**


$$\begin{array}{c} Bu^tC{\equiv}P \\ \downarrow \\ Pt(PPh_3)_2 \end{array}$$

**4**

In the $\eta^2$-complex (**4**) [6] however, this bond is considerably elongated (up to 1.672(17) Å) as compared with the corresponding value in the free ligand. It should be emphasized that the same picture is also observed in phosphaalkenes $R_2C{=}PR'$; the double P=C bond remaining almost unchanged on formation of $\eta^1$-complexes; whereas in $\eta^2$-complexes

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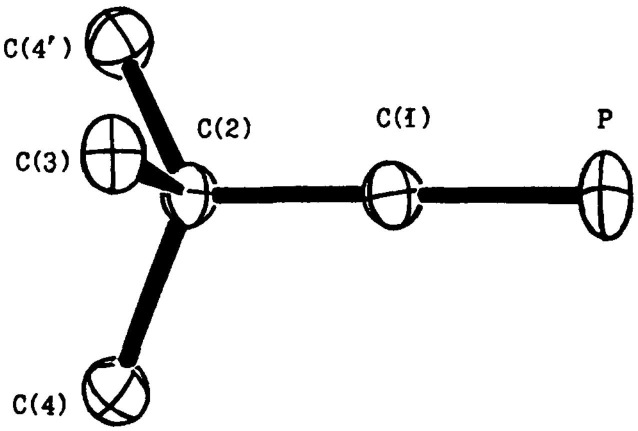

**FIGURE 1.** General view of the molecular structure of **2** including the numbering scheme. The atoms P, C(1), C(2), and C(3) occupy a crystallographic mirror plane. Geometrical parameters of **2**: P–C(1) 1.542(2), C(1)—C(2) 1.470(3), C(2)–C(3) 1.539(2), C(2)–C(4) 1.537(2) Å, PC(1)C(2) 179.3(2), C(1)C(2)C(3) 109.7(2), C(1)C(2)C(4) 109.1(1), C(3)C(2)C(4) 109.3(2), C(4)C(2)C(4′) 110.3(2)°, PC(1)C(2)C(4) −60.3(1)°.

it is substantially elongated [7]. The C(1)–C(2) bond length (1.470(3) Å) is quite normal for a C(sp)–C($sp^3$) bond distance [8], and the C(2) atom has an almost ideal tetrahedral environment with the bond angles CCC in the range 109.1–109.7° (avg 109.5(2)°).

Molecules (**2**) are kept within the crystal by means of normal Van der Waals interactions. No shortened intermolecular contacts are observed, the shortest P···C, P···H, C···C and C···H distances being 3.805(2), 3.43(4), 3.956(3), and 2.64(4) Å, respectively (corresponding sums of Van der Waals radii are 3.60, 3.10, 3.40, and 2.90 Å [9]). It is noteworthy that the P≡C and C–C(Bu$^t$) bond lengths reported earlier in the microwave spectroscopic study of (**2**) (1.536 and 1.473 Å [3c]) are very close to the values found in the present work.

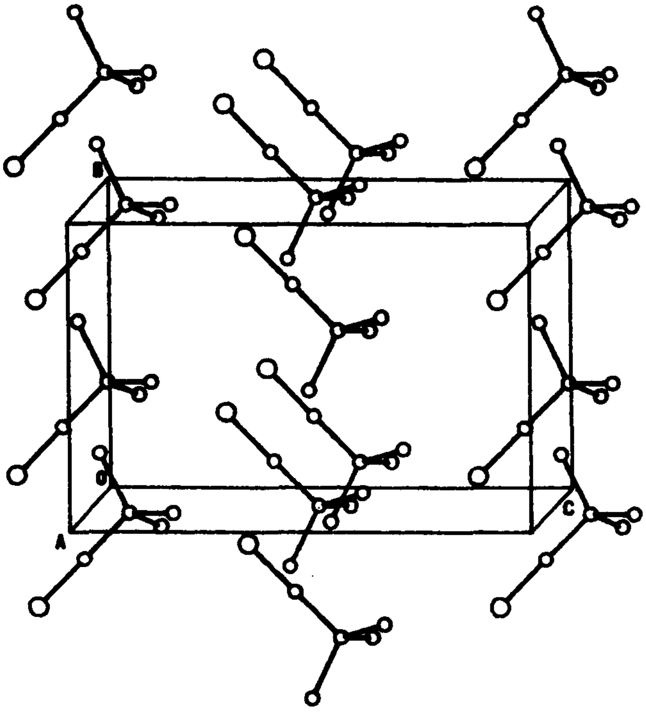

**FIGURE 2.** Packing diagram of **2**.

## EXPERIMENTAL

The single crystal of the liquid (**2**) suitable for X-ray diffraction study was grown in a thin-walled capillary (diameter ca. 0.5 mm) by very slowly cooling its melt near the melting point at 193 K.

*Crystal Data.* $PC_5H_9$, $M = 100.1$, orthorhombic, $a = 8.662(2)$, $b = 7.072(7)$, $c = 10.569(1)$ Å, $V = 647.4$ Å$^3$, $Z = 4$, $d_c = 1.03$ g/cm$^3$, space group Cmc$2_1$ (No. 36), $\mu = 2.9$ cm$^{-1}$, $F(000) = 216$.

Crystallographic measurements were made at 108 K using an Enraf Nonius CAD-4 diffractometer operating in the $\omega$-$2\theta$ scan mode (the ratio of the scanning rates was $\omega/\theta = 1{:}2$). The intensity data were collected within the range $1 \leq \theta \leq 31°$ using graphite-monochromated Mo–K$\alpha$ radiation ($\lambda = 0.71073$ Å). Intensities of 1136 reflections (579 of them unique) were measured and the structure was solved by direct methods and refined by full-matrix least-squares. In the refinement 498 reflections with $I > 3\sigma$ were used.

All hydrogen atoms were located in the difference Fourier maps and refined isotropically. Convergence was obtained at $R = 0.03285$ and $Rw = 0.03897$ (for the inverted structure $R = 0.03297$ and $Rw = 0.03935$). Corrections for Lorentz and polarization effects were applied but not for absorption. Calculations were performed using the SDP-PLUS program. Coordinates and temperature factors of all atoms are deposited at the Cambridge Crystallographic Data Centre [10].

## ACKNOWLEDGMENT

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## REFERENCES

[1] Cambridge Crystallographic Data Base (release 1989).
[2] A. M. Arif, A. R. Barron, A. H. Cowley, S. W. Hall, *J. Chem. Soc. Chem. Commun.*, 1988, 171.
[3] [a] H. W. Kroto, *Chem. Soc. Rev.*, *11*, 1982, 435; [b] J. C. T. R. Burkett-St. Laurent, T. A. Cooper, H. W. Kroto, J. F. Nixon, O. Ohashi, K. Ohno, *J. Mol. Struct.*, *79*, 1982, 215; [c] H. Oberhammer, G. Becker, G. Gresser, *J. Mol. Struct.*, *75*, 1981, 283.
[4] J. F. Nixon, *Chem. Revs.*, *88*, 1988, 1327; M. Regitz, P. Binger, *Angew. Chem. 100*, 1988, 1541; *Angew. Chem. Int. Ed.*, *27*, 1988, 1484.

[5] P. B. Hitchcock, M. J. Maah, J. F. Nixon, J. A. Zora, G. J. Leigh, M. A. Bakar, *Angew. Chem. Int. Ed.*, *99*, 1987, 497; *Angew. Chem.*, *26*, 1987, 474.
[6] J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, H. W. Kroto, J. F. Nixon, *J. Chem. Soc. Chem. Commun.*, 1981, 1141.
[7] A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, *Zh. Strukt. Khim.*, (*J. Struct. Chem.*, Russian trans.), *29*, N2, 1988, 122.
[8] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. II*, 1987, S.1.
[9] L. Pauling: *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, N.Y., 1960.
[10] CCDC, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.