

1,2,4-Azadiphosphole

A. S. Ionkin,* S. N. Ignat'eva, I. A. Litvinov, V. A. Naumov, and
B. A. Arbuzov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the USSR
Academy of Sciences, A. E. Arbuzov Street, 8, Kazan 420083, USSR

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ABSTRACT

tert-Butylaminophosphaalkyne **4** is shown to dimerize in alkaline medium to 1-*tert*-butyl-3-*tert*-butylamino-1,2,4-azadiphosphole **1**—the first representative of 1,2,4-azadiphospholes. The structure of **1** has been determined by IR and ^{31}P NMR spectroscopy and by X-ray crystallography. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.356(7)$, $b = 11.817(5)$, $c = 11.830(3)$ Å, $\alpha = 88.51(3)$, $\beta = 78.61(4)$, $\gamma = 77.05(4)^\circ$, $V = 1383(1)$ Å 3 , $Z = 4$ (two independent molecules).

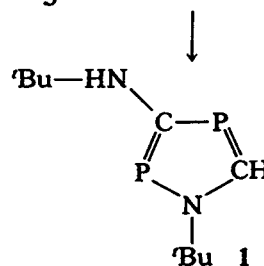
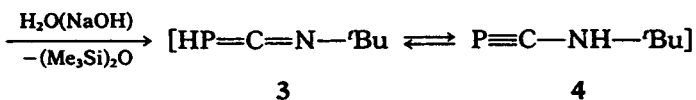
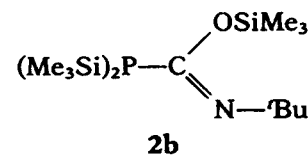
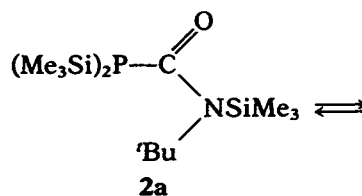
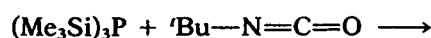
INTRODUCTION

In the literature there are described syntheses of heterosubstituted (e.g., $\text{P}\equiv\text{C}-\text{F}$ [1], $\text{P}\equiv\text{C}-\text{NR}_2$ [2, 3]) and carbosubstituted ($\text{P}\equiv\text{C}-\text{R}$ [4]) phosphalkynes, each of which has a tendency to undergo oligomerization. Remarkably, however, unlike nitriles $\text{N}\equiv\text{C}-\text{R}$ that are known to be capable of trimerizing to *s*-triazines [5], the analogous carbosubstituted phosphalkynes undergo tetramerization and pentamerization [6].

We have now found that *tert*-butylaminophosphaalkyne **4** dimerizes in alkaline medium to form 1-*tert*-butylamino-1,2,4-azadiphosphole **1**.

RESULTS AND DISCUSSION

For the preparation of *tert*-butylaminophosphaalkyne **4** the compounds **2a**, **2b** were synthesized according to the procedure of R. Appel et al. [2]. The subsequent elimination of siloxane and replacement of the trimethylsilyl group by the hydrogen atom were carried out in one pot using moist sodium hydroxide. The formation of **1** can reasonably be explained as follows:



*To whom correspondence should be addressed.

The phosphallene **3** formed, rearranges to *tert*-butylaminophosphaalkyne **4** via a 1,3-H-shift (cf. [2]). As a further intermediate a 1H-azaphosphirene is suggested by MNDO calculations [7]. Interaction of the intermediates results in the formation of compound **1**—the first of the 1,2,4-azadiphospholes related to the known 1,2,4-thiadiphosphole [8] and 1,2,3-azadiphosphole [9].

The structure of **1** has been confirmed by ^{31}P NMR and IR spectral data and by X-ray structural analysis. Thus, in the ^{31}P NMR spectrum of **1** there are observed two signals with $\delta_{\text{p}} + 115.9$ (P-4) and $+ 169.0$ (P-2). In the IR spectrum of **1** there is present a narrow band at 3365 cm^{-1} , characteristic of N–H bond vibrations, with no absorption of a P–H bond.

According to X-ray crystal structure analysis, two independent molecules A and B in a single crystal of **1** appeared to have similar geometries. Therefore, only one of them (molecule A) is shown in Figure 1. Many of the bond lengths and bond angles of the molecules A and B differ significantly (Table 1). These differences are possibly due to the poor quality of the investigated crystal.

Mean values of the geometrical parameters are used in the discussion of results.

Similarly to five-membered heterocycles in 1,2,3 σ^2 -diazaphospholes and 1,2,4,3 σ^2 -triazaphospholes [10], which were shown to be planar with averaged bond lengths due to the π -electron delocalization, the five-membered heterocycle in the molecule of **1** is also planar within 0.02 \AA . The endocyclic nitrogen atom N(1) adopts a trigonal planar configuration, whereas the exocyclic tetrahedral atom N(3) together with the C(6) atom are in the plane of the heterocycle. Unlike $\text{P}(4)=\text{C}(5)$ ($1.742(8)\text{ \AA}$), the $\text{P}(2)=\text{C}(3)$ interatomic distance ($1.712(7)\text{ \AA}$) in **1** is slightly shorter than the $\text{P}=\text{C}$ double bond in diazaphospholes (1.75 \AA [10]). The $\text{P}(4)-\text{C}(3)$ bond ($1.770(7)\text{ \AA}$) is shorter than the corresponding bond in acyclic compounds having a two-coordinated phosphorus atom ($1.82\text{--}1.86\text{ \AA}$). Being compared with the corresponding bond both in diazaphospholes ($1.65\text{--}1.68\text{ \AA}$) and in acyclic compounds with the two-coordinated phosphorus atom (1.76 \AA), the $\text{N}(1)-\text{P}(2)$ bond ($1.778(7)\text{ \AA}$) appears to be elongated, probably due to the bulky substituent at the N(1) atom. A value for the $\text{N}(1)-\text{C}(5)$ bond length ($1.300(8)\text{ \AA}$) has good consistency with that for the conjugated bond. Thus, on the whole, the bond lengths found favor a conjugation in the heterocycle of molecule **1**.

Values of bond angles at both phosphorus atoms vary from $93.9(3)^\circ$ to $99(3)^\circ$, being almost equal to those in acyclic compounds with two-coordinated phosphorus ($95^\circ\text{--}113^\circ$) but larger than those in cyclic diazaphospholes ($88.5^\circ\text{--}92.0^\circ$).

Because of the large thermal vibrations of *tert*-butyl groups, their geometrical parameters were determined with substantial errors.

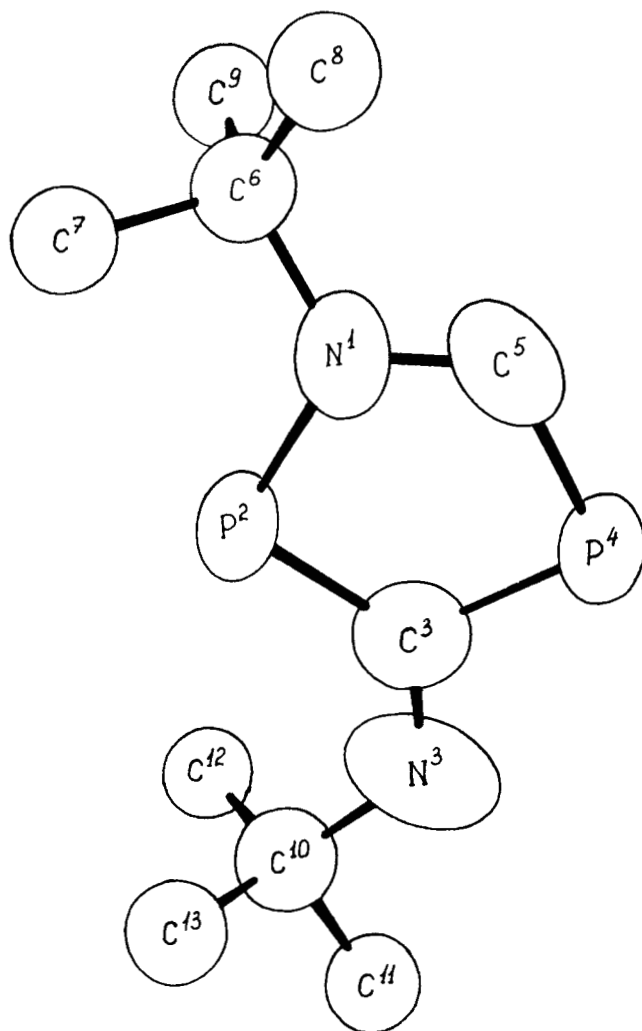


FIGURE 1 Atomic numbering scheme for molecule **1** in crystal. Atoms of *t*-butyl groups are shown with arbitrary radii ($B_{\text{iso}} = 5\text{ \AA}^2$). H-atoms are not shown.

It should also be noted that molecules **1** form centrosymmetrical pairs with the following distances and angles: $\text{N}(3)\cdots\text{P}(4)'$ [$-x, 1 - y, -z$] 3.392 \AA , $\text{H}(3)\cdots\text{P}(4)'$ 3.03 \AA , $\text{N}(3)-\text{H}(3)\cdots\text{P}(4)'$ 158° (all for molecule A), $\text{N}(3)\cdots\text{P}(4)''$ [$1 - x, -y, 1 - z$] 3.827 \AA , $\text{H}(3)\cdots\text{P}(4)''$ 2.82 \AA , $\text{N}(3)-\text{H}(3)\cdots\text{P}(4)''$ 152° (all for molecule B). Therefore, hydrogen bonding of the $\text{N}-\text{H}\cdots\text{P}$ type seems likely to exist in the crystal of **1**.

EXPERIMENTAL

^{31}P NMR spectra were recorded on a Bruker M-250 spectrometer. IR spectra were obtained on a UR 20 spectrophotometer.

TABLE 1 Coordinates of Non-H-atoms for Structure 1

$$B_{\text{iso}}^{\text{eqv}} = 4/3 \sum_{i=1}^3 \sum_{j=1}^3 (\hat{a}_i \hat{a}_j) B(i, j) \text{ (Å}^2\text{)}$$

Molecule A				
Atom	X	Y	Z	$B_{\text{iso}}^{\text{eqv}}$
P(2)	0.0219(2)	0.6815(2)	0.3142(2)	6.03(6)
P(4)	0.0768(2)	0.4849(2)	0.1507(2)	5.37(5)
N(1)	0.1575(7)	0.5568(6)	0.3248(6)	6.3(2)
N(3)	-0.1208(8)	0.6685(7)	0.1496(7)	8.8(2)
C(3)	-0.0214(8)	0.6243(8)	0.2007(7)	6.3(2)
C(5)	0.1825(9)	0.4750(7)	0.2513(8)	6.7(3)
C(6)	0.2471(7)	0.5563(7)	0.4136(6)	5.3(2)
C(7)	0.161(1)	0.610(1)	0.523(1)	14.0(4)
C(8)	0.312(1)	0.442(1)	0.445(1)	13.5(4)
C(9)	0.345(1)	0.630(1)	0.365(1)	12.4(4)
C(10)	-0.2209(8)	0.7867(8)	0.1799(8)	6.4(2)
C(11)	-0.303(1)	0.792(1)	0.088(1)	14.6(5)
C(12)	-0.161(1)	0.8855(9)	0.171(1)	9.3(3)
C(13)	-0.3071(9)	0.780(1)	0.2957(9)	8.8(3)
Molecule B				
Atom	X	Y	Z	$B_{\text{iso}}^{\text{eqv}}$
P(2)	0.4759(2)	0.1846(2)	0.1806(2)	5.37(5)
P(4)	0.5708(2)	0.1389(2)	0.4003(2)	5.87(6)
N(1)	0.6208(6)	0.2300(5)	0.1948(5)	4.8(2)
N(3)	0.3461(7)	0.0802(6)	0.3661(6)	6.5(2)
C(3)	0.4491(8)	0.1305(8)	0.3176(7)	5.5(2)
C(5)	0.6644(8)	0.2068(7)	0.2937(7)	5.3(2)
C(6)	0.6952(7)	0.2896(7)	0.1021(7)	5.7(2)
C(7)	0.632(1)	0.313(1)	0.002(1)	14.1(4)
C(8)	0.693(2)	0.408(1)	0.140(1)	15.4(4)
C(9)	0.830(1)	0.232(1)	0.067(1)	20.0(5)
C(10)	0.2360(8)	0.0580(7)	0.3138(8)	5.8(2)
C(11)	0.1561(9)	0.1663(9)	0.276(1)	9.1(3)
C(12)	0.291(1)	-0.0260(9)	0.215(1)	9.7(3)
C(13)	0.147(1)	0.008(1)	0.407(1)	9.9(3)

Reaction of Tris(trimethylsilyl)phosphine with tert-Butylisocyanate

A solution of 20 g (80 mmol) of tris(trimethylsilyl)phosphine and 10.2 g (103 mmol) of tert-butylisocyanate in 25 mL of diethyl ether was refluxed under a stream of argon for 2 weeks, the progress of reaction being checked by ^{31}P NMR. After removal of the solvent the residue was distilled to give 17.7 g (63%) of the tautomeric mixture **2a**, **2b** as a pale yellow labile liquid: $\delta_{\text{P}} = -115$ and -133 .

1-tert-Butyl-3-tert-butylamino-1,2,4-azadiphosphole (1)

Finely ground moist sodium hydroxide (2.5 g) was added in small portions to solutions of 15.3 g of **2a**, **2b** in 38 mL of THF. When heated, the solution

turned deep red. The reaction mixture was kept in a bath at 55°C for 1.5 h; at this time the reaction appeared to be complete by ^{31}P NMR spectroscopy. The solvent and the siloxane formed were collected in a trap maintained at -78°C . Distillation of the residue at $94^\circ\text{C}/0.01$ mm gave 1.1 g (13%) of **1** with mp 83°C . Anal. calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{P}_2$ N 12.17; P 26.95. Found: N 12.0; P 27.1.

X-Ray Structure Determination for 1

A single crystal of **1** was obtained by recrystallization from pentane.

A summary of the structure determination carried out at room temperature is given in Table 2. Bond lengths and bond angles are listed in Tables 3 and 4, respectively. The structure of **1** showing the atom numbering scheme is given in Figure 1.

TABLE 2 Structure Determination Summary for **1** at 25°C

Empirical formula	C ₁₀ H ₂₀ N ₂ P ₂
Color; habit	Yellow prisms
Crystal size	0.2 × 0.1 × 0.1 (mm)
Crystal system	Triclinic
Space group	P1
Unit cell dimensions (from 25 high angle reflections)	<i>a</i> = 10.356(7) Å <i>b</i> = 11.817(5) Å <i>c</i> = 11.830(3) Å α = 88.51(3)° β = 78.61(4)° γ = 77.05(4)°
Volume <i>V</i>	1383(1) Å ³
<i>Z</i>	4 (two independent molecules)
Formula weight	230.23
Density (calc)	1.11 g cm ⁻³
Absorption coefficient	2.79 cm ⁻¹
F(000)	496
Diffractometer used	Enraf Nonius CAD4
Radiation	MoK α (λ = 0.71073 Å) graphite monochromator
2 θ range	4°–50°
Scan mode	ω /(5/3 θ)
Scan speed	Variable: 2°–20° min ⁻¹ in σ (<i>I</i>)
Scan range (ω)	Variable: ω = (1.35 + 0.35 tg θ)°
Standard reflections	Two intensity and two orientation control reflections measured every 200 reflections
Index ranges	–10 ≤ <i>h</i> ≤ 10, –12 ≤ <i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 12
Reflections collected	4552
Observed reflections	1582
System	SDP-PLUS PDP-11/23
Solution	Direct methods
Refinement method	Full-matrix least squares (on F's)
Quantity minimized	$\sum \omega(F_o - F_c)^2$
Hydrogen atoms	not refined, fixed <i>B</i> (iso) = 4.0 Å ²
Weighting scheme	$\omega = 4 F_o ^2/((\sigma(I))^2 + (0.07 F_o ^2)^2)$
Final R indices (observed data)	R = 0.063, wR = 0.087
Goodness of fit	2.1
Largest Δ/δ	0.64
Data to parameter ratio	6.24
Largest difference peak	0.5 eÅ ⁻³

TABLE 3 Distances (Å) with Estimated Standard Deviations in Parentheses for **1**

Bond	Molecule A	Molecule B	Bond	Molecule A	Molecule B
P(2)—N(1)	1.814(6)	1.741(5)	N(3)—H(3)	0.95	1.10
P(2)—C(3)	1.699(7)	1.721(6)	C(5)—H(5)	1.25	1.28
P(4)—C(3)	1.778(7)	1.762(7)	C(6)—C(7)	1.48(1)	1.45(1)
P(4)—C(5)	1.754(8)	1.729(7)	C(6)—C(8)	1.44(1)	1.48(1)
N(1)—C(5)	1.265(8)	1.335(7)	C(6)—C(9)	1.50(1)	1.39(1)
N(1)—C(6)	1.532(8)	1.471(7)	C(10)—C(11)	1.50(1)	1.472(9)
N(3)—C(5)	1.298(8)	1.359(7)	C(10)—C(12)	1.43(1)	1.49(1)
N(3)—C(10)	1.544(9)	1.474(8)	C(10)—C(13)	1.49(1)	1.49(1)

TABLE 4 Bond Angles^a with Estimated Standard Deviations in Parentheses for 1

Angle	Molecule A	Molecule B
N(1)P(2)C(3)	99.7(3)	94.7(3)
C(3)P(4)C(5)	94.3(3)	93.9(3)
P(2)N(1)C(5)	118.2(5)	117.3(4)
P(2)N(1)C(6)	120.5(4)	122.3(4)
C(5)N(1)C(6)	121.1(6)	120.4(5)
C(3)N(3)C(10)	125.7(7)	128.2(5)
P(2)C(3)P(4)	115.8(4)	115.9(4)
P(2)C(3)N(3)	127.5(6)	126.5(5)
P(4)C(3)N(3)	116.6(6)	117.7(5)
P(4)C(5)N(1)	117.9(6)	118.2(5)
N(1)C(6)C(7)	108.7(6)	113.9(6)
N(1)C(6)C(8)	114.7(6)	110.3(6)
N(1)C(6)C(9)	106.2(6)	112.9(7)
C(7)C(6)C(8)	104.7(8)	101.9(9)
C(7)C(6)C(9)	109.6(8)	110(1)
C(8)C(6)C(9)	112.9(8)	108(1)
N(3)C(10)C(11)	100.4(7)	111.4(6)
N(3)C(10)C(12)	115.3(6)	110.2(6)
N(3)C(10)C(13)	109.0(6)	105.5(6)
C(11)C(10)C(12)	108.9(8)	110.3(7)
C(11)C(10)C(13)	110.2(7)	108.7(7)
C(12)C(10)C(13)	112.3(7)	110.6(6)

SUPPLEMENTARY MATERIAL AVAILABLE

Lists of structure factors, atomic coordinates, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre. Copies may be obtained through the Ex-

ecutive Secretary, International Union of Crystallography, 5 Abby Square, Chester CY1 2YU, England.

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