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Structural Evidence for P_π-P_π Conjugation in Aminosubstituted Phosphaalkynes

Alexander N. Chernega,* Georg N. Koidan,
and Anatoly P. Marchenko

Institute of Organic Chemistry of the Academy of Sciences of the Ukraine, Murmanskaya St. 5, Kiev-94, 253660, Ukraine

Anatoly A. Korkin**

Institut für Organische Chemie, Henkestr. 42, D-8520, Erlangen, Germany

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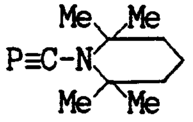
ABSTRACT

The molecular structure of 2,2,6,6-tetramethylpiperidinophosphaalkyne was determined by the X-ray structural method. The main geometrical parameters are as follows: $P\equiv C$ *1.559(2), N–C(sp) 1.316(2) Å,* $P\equiv C$*–N 178.9(1)°, with an almost planar trigonal bond configuration for the N atom and the chair conformation of the piperidine ring. Structural evidence for the nitrogen lone pair conjugation with the π-system of the triple bond was found to be different in phosphaalkynes* $P\equiv C{-}NR_2$ *and nitriles* $N\equiv C{-}NR_2$*. Quantum-chemical ab initio calculations (HF/6-31G*) showed that this is caused by a different character of polarization of the* $P\equiv C$ *and* $N\equiv C$ *triple bonds.*

INTRODUCTION

Recently, we have considered structural and energetic consequences of P_π-P_π conjugation of the nitrogen lone pair (LP(N)) with the P=C double bond on the basis of experimental X-ray structural data for aminosubstituted phosphaalkenes and *ab initio* quantum-chemical calculations of model systems [1]. As a continuation of this work, we felt that a study of peculiarities of the LP(N) interaction with the $P\equiv C$ triple bond would be of interest. In this connection, we carried out an X-ray structural investigation of the recently synthesized [2] 2,2,6,6-tetramethylpiperidinophosphaalkyne **1**, and the experimental data obtained were compared with results of *ab initio* quantum-chemical calculations for model molecules. We should note that hitherto the molecular structure of aminosubstituted phosphaalkynes has not been investigated by any structural methods.



1

$P\equiv C{-}Bu^t$

2

RESULT AND DISCUSSION

Structural Data

The molecular structure of compound **1** is represented in Figure 1, and its crystal packing is shown in Figure 2. The main geometrical parameters of **1** are given in Table 1.

The bond lengths distribution in the P–C–N moiety is the most interesting feature in the molecular structure of **1**. Thus, the $P\equiv C$ triple bond, 1.559(2) Å, in **1** is noticeably (by 0.017(2) Å) elon-

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*To whom correspondence should be addressed.

**Currently Alexander von Humboldt Fellow, Institute of Physiologically Active Substances, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia.

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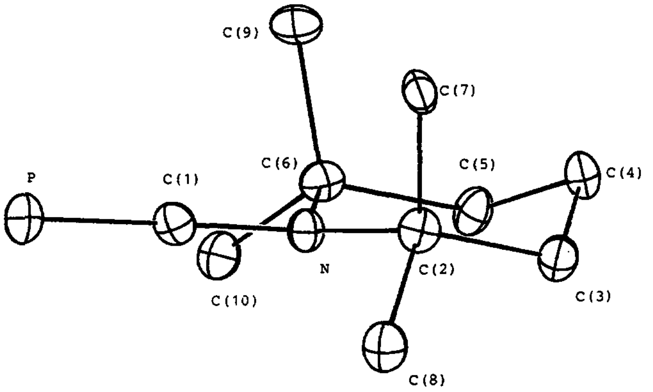

FIGURE 1 General view of molecule **1** with the numbering scheme (H atoms omitted for clarity).

gated in comparison to 1.542(2) Å in compound **2** [3]. On the other hand, the C(1)–N bond, 1.316(3) Å, is considerably shortened in comparison to the range of 1.42–1.45 Å which is characteristic for purely single C(sp^2)–N(sp^2) bonds [4] (the decrease in atom C covalent radii on going from sp^2- to sp-hybridization state is only ~0.03–0.05 Å [5]). In fact, it is close to the C–N bond length 1.34 Å with a bond order of 1.5 [4a]. The bond configuration of the N atom is close to trigonal planar—the sum of the bond angles is 355.2(3)°. All these structural data together show a considerable effect of n_N-$\pi_{P\equiv C}$ conjugation:

$$\underset{(a)}{E\equiv C{-}NR_2} \leftrightarrow \underset{(b)}{E{=}C{=}NR_2}$$

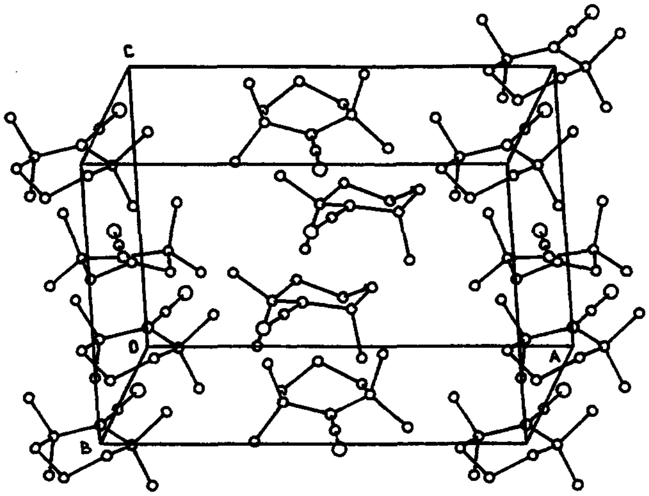

FIGURE 2 Molecular packing in crystal **1**.

TABLE 1 Selected Bond Lengths (Å) and Bond Angles (°) in **1**

P–C(1)	1.559(2)	C(1)NC(2)	116.4(1)
N–C(1)	1.316(2)	C(1)NC(6)	115.0(1)
N–C(2)	1.513(2)	C(2)NC(6)	123.8(1)
N–C(6)	1.514(2)	PC(1)N	178.9(1)
C(2)–C(3)	1.528(3)	NC(2)C(3)	110.1(1)
C(3)–C(4)	1.525(2)	C(2)C(3)C(4)	112.9(1)
C(4)–C(5)	1.511(3)	C(3)C(4)C(5)	108.5(1)
C(5)–C(6)	1.535(2)	C(4)C(5)C(6)	113.3(1)
		NC(6)C(5)	109.6(1)

The experimental data on structural consequences of conjugation in phosphaalkynes given above are in good accordance (both qualitative and quantitative) with the results of *ab initio* calculations for the model molecules $P\equiv C{-}CH_3$ and $P\equiv C{-}NH_2$ [6]. Indeed, these calculations showed that n_N-$\pi_{P\equiv C}$ conjugation causes elongation of the phosphorus-carbon triple bond by 0.016 Å (from 1.553 to 1.569 Å).

It is important to note that the above-mentioned structural consequences of P_π-P_π conjugation in phosphaalkynes are clearly different from those observed in the isovalent isomeric nitriles $N\equiv C{-}R$. In fact, according to experimental data [7], the length of the $N\equiv C$ triple bond is not essentially changed in these compounds on going from $R = CH_3$ to $R = NH_2$ and $N(CH_3)_2$ (1.159(2), 1.160(5), and 1.161(2) Å, respectively). In addition, the $(N\equiv)C{-}N(sp^2)$ bond in two later nitriles (1.346(5) and 1.338(2) Å) is noticeably longer than in **1**.

The piperidine ring has a slightly distorted chair conformation: the C(2), C(3), C(5), and C(6) atoms are coplanar (deviations of atoms from the mean-square plane do not exceed 0.002 Å). The "edges" NC(2)C(6) and C(3)C(4)C(5) form dihedral angles 149.4(2) and 125.6(2)° with this plane. Torsion angles in the ring are as follows: NC(2)C(3)C(4) −46.5(2), C(2)C(3)C(4)C(5) 62.1(3), C(3)C(4)C(5)C(6) −62.3(3), C(4)C(5)C(6)N 46.7(2), C(5)C(6)NC(2) −34.1(3), C(6)NC(2)C(3) 34.2(3). Distribution of the bond length and bond angles in the piperidine ring is unexceptional (av N–C 1.514(2), C–C 1.525(3) Å, CNC 123.8(1), NCC 109.9(1)°).

Molecules **1** are kept within the crystal by means of normal van der Waals interactions. No shortened intermolecular contacts are observed. The shortest P. . .P, P. . .C, C. . .C, and C. . .H distances are 5.8776(6), 3.693(2), 3.690(2), and 3.05(2) Å, respectively (corresponding sums of van der Waals radii are 3.80, 3.60, 3.40, and 2.90 Å [8]).

Quantum-Chemical Calculations

To elucidate the reasons for considerable differences in structural consequences of n_N-π conjugation experimentally observed in phosphaalkynes and nitriles, we performed *ab initio* (HF/6-31G*) quantum-chemical calculations of model molecules 3–6 with complete geometry optimizations and calculations for molecules **4** and **6** assuming ideal linearity of the $P\equiv C{-}N$ group and planar tri-

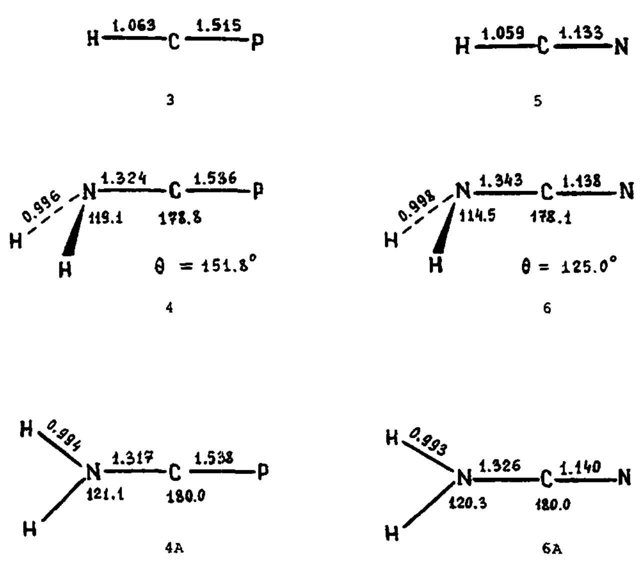

FIGURE 3 Optimized geometries of model molecules 3–6 (in molecules **4A** and **6A** amino-group fixed as planar). ϑ is the dihedral angle between the CNH planes.

gonal bond configuration for the N atom (molecules **4A** and **6A**, respectively). Results of calculations are represented in Figure 3 and Table 2.

$$\mathrm{P{\equiv}C{-}R} \qquad \mathrm{N{\equiv}C{-}R}$$
$$\mathrm{R = H\ (\mathbf{3}),\ NH_2\ (\mathbf{4})} \quad \mathrm{R = H\ (\mathbf{5}),\ NH_2\ (\mathbf{6})}$$

As one may see from Figure 3, the P≡C bond length in **3** estimated at the HF/6–31* level is somewhat shorter than the experimental value of 1.540–1.542 Å obtained for this molecule from the MW spectrum [9]. Basis set and electron correlation effects on the geometry of **3** have been considered previously [6a,10]. However, insofar as the aim of our calculations was only a consideration of relative structural effects, we believe that the HF/6–31* level is just sufficient. In fact, our calculations qualitatively reproduce experimentally observed changes in geometry rather well: for phosphaalkynes, the triple bond is elongated noticeably (by 0.021 Å) from **3** to **4**, while for nitriles, it is changed only slightly from **5** to **6** (elongated by only 0.005 Å). The C(sp)–N bond in **6** (1.343 Å) is noticeably longer than in **4** (1.324 Å), in accordance with experiment. These structural differences between phosphaalkynes and nitriles are clearly caused by the fact that H → NH_2 substitution brings to a triple bond both conjugation and polar effects. Structural consequences are always the sum of these two factors. Conjugation should cause a shortening of the N–C bond and an elongation of the triple bond, both for phosphaalkynes and for nitriles. However, as a result of different polarity directions of the P≡C and N≡C triple bonds, the effect of polarization is manifested in different ways for these compounds. Indeed, in **3**, the charge on the P atom is positive and the charge on the C atom is negative, while in **5**, the picture is reversed. Therefore, for nitriles, polarization of the triple bond increases from **5** to **6** (the absolute $q_N q_C$ value increases from −0.041 to −0.212). This effect favors shortening of this bond and, consequently, compensates for a large part of the conjugation effect. Inversely, in phosphaalkynes, the H → NH_2 substitution causes a considerable decrease of the P≡C bond polarization (the absolute $q_P q_C$ value decreases from −0.427 in **3** to −0.105 in **4**). Consequently, the polarization also favors elongation of the triple bond in phosphaalkynes, combining with the conjugation effect.

TABLE 2 Net Charges,[a] Bond Orders,[b] and Ionization Potential (eV) for Model Molecules **3–6**

Molecule N	Molecule E≡C–X	q_E	q_C	q_X	$q_{E\equiv C}$	q_{C-X}	IP
3	P≡C–H	0.540	−0.791	0.250	2.479	0.737	10.45
4	P≡C–NH_2	0.345	−0.305	−0.040	2.471	0.907	8.46
5	N≡C–H	−0.349	0.117	0.232	2.657	0.761	13.52
6	N≡C–NH_2	−0.429	0.494	−0.066	2.554	0.896	11.29

[a]Atomic charges are defined for NAO [14a,b].

[b]NLMO/NPA bond orders as defined by Reed and Schleyer [14c].

As seen both from experimental data and from calculations, n_N-$\pi_{E\equiv C}$ conjugation causes flattening of the N atom pyramid in phosphaalkynes to a much greater extent than in nitriles. It is noteworthy that planarization of the N atom requires 1.5 kcal/mol in **6**, while only 0.2 kcal/mol is required in **4**. Obviously, the higher degree of nitrogen planarization is one of the main factors that causes the above-mentioned C(sp)–N bond shortening in phosphaalkynes. Indeed, in ideally flattened molecules **4A** and **6A**, this difference is only 0.009 Å (Figure 3).

One may note that H → NH_2 substitution decreases ionization potentials in both types of compounds considered (see Table 2). Among the other electron structure peculiarities, it is worthwhile to note the different character of LP(P) in phosphaalkynes and nitriles: the natural atomic orbitals (NAO), corresponding to LP(P), have 74 and 76% of s-AO contribution in **5** and **6** and only 50 and 52% in **3** and **4**.

EXPERIMENTAL

A single crystal of compound **1** suitable for X-ray diffraction study was grown in a thin-walled capillary (ca. 0.5-mm diameter) by very slow cooling of its melt near the mp ca. −15 to −18°C. The resulting crystal was slowly cooled to −140°C, and at this temperature, an X-ray diffraction experiment was carried out.

Crystal data for **1**: $C_{10}H_{18}NP$, M = 183.2, orthorhombic, a = 8.874(4), b = 9.205(4), c = 13.230(4)

TABLE 3 Coordinates of Nonhydrogen Atoms and Their Equivalent Isotropic Temperature Factors B_{eq} (Å^2) in Structure **1**

Atom	*x*	*y*	*z*	B_{eq}
P	−0.59789(7)	−0.05184(7)	−0.95313(4)	2.62(1)
N	−0.9108(2)	−0.0372(2)	−1.0083(1)	1.83(3)
C(1)	−0.7679(3)	−0.0436(2)	−0.9821(1)	2.25(4)
C(2)	−1.0220(3)	−0.0041(2)	−0.9247(2)	2.15(4)
C(3)	−1.1831(2)	−0.0229(3)	−0.9634(1)	2.56(4)
C(4)	−1.2092(3)	0.0492(3)	−1.0657(2)	2.82(4)
C(5)	−1.1073(3)	−0.0224(3)	−1.1425(2)	2.61(4)
C(6)	−0.9390(2)	−0.0037(2)	−1.1187(1)	2.02(3)
C(7)	−0.9967(3)	0.1497(2)	−0.8848(2)	2.55(4)
C(8)	−0.9947(3)	−0.1133(2)	−0.8400(2)	2.58(4)
C(9)	−0.8877(3)	0.1520(3)	−1.1420(2)	2.67(4)
C(10)	−0.8506(3)	−0.1130(3)	−1.1817(2)	2.62(4)

Å, V = 1080.7 Å^3, $Z = 4$, $d_c = 1.13$ g cm^{-3}, space group $P2_12_12_1$, $\mu = 18.5$ cm^{-1}, F(000) = 400.

Crystallographic measurements were made using an Enraf Nonius CAD-4 diffractometer operating in the $\omega/2\theta$ scan mode (the ratio of the scanning rates $\omega/\theta = 1.2$). The intensity data were collected within the range $2 \leq \theta \leq 70°$ using graphite monochromated Cu-K_α radiation (λ = 1.54184 Å). Intensities of 1069 unique reflections were measured. The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation. The weighting scheme $w = (\sigma^2F + 0.0016F^2)^{-1}$ was used. In the refinement, 955 reflections with $I > 3\sigma(I)$ were used. All hydrogen atoms were located in the difference Fourier maps and refined isotropically. Convergence was obtained at $R = 0.041$ and $R_w = 0.058$, GOF = 2.90 (for the inverted structure $R = 0.047$, $R_w = 0.070$). Corrections for Lorentz and polarization effects but not for absorption were applied. The final atomic coordinates and equivalent isotropic temperature factors are given in Table 3. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [11]. Full crystallographic data have been deposited at the Cambridge Crystallographic Data Centre [12].

The *ab initio* MO LCAO SCF calculations of the model molecules 4–6 have been performed with the GAUSSIAN 90 program package [13] at the HF/6-31G* level with full geometry optimization. The NAO charges and NLMO/NPA bond orders have been obtained from NBO analysis [14] incorporated in G90.

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