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First structural characterization of an α-diazophosphane: crystal structure of bis[bis(diisopropylamino)phosphanyl]diazomethane $[(i\text{-}Pr_2N)_2P]_2CN_2$

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Abstract

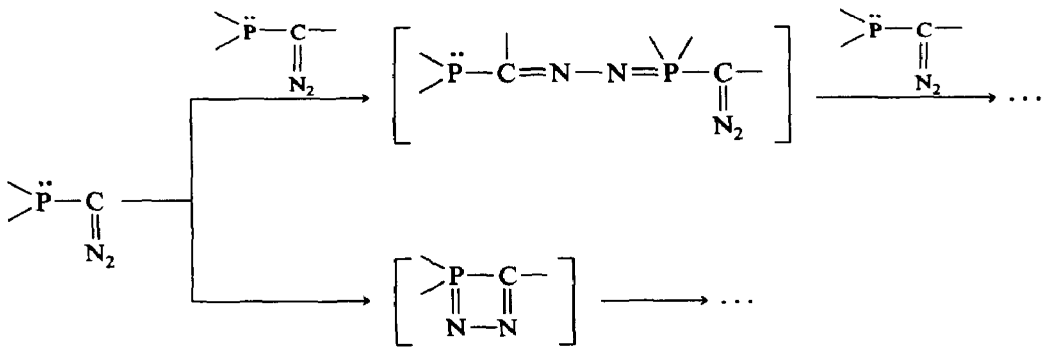
Crystals of bis[bis(diisopropylamino)phosphanyl]diazomethane $P_2N_6C_{25}H_{56}$, M = 502.7 belong to the monoclinic space group, $C2/c$ with a 12.044(2), b 28.661(4), c 10.301(1) Å, β 116.13(1)°, V 3192(2) Å^3 and $Z = 4$. The structure was refined by use of 1275 non zero Mo-K_α reflections to $R = 0.052$ at 293 K. The unit cell contains discrete monomeric molecules. The structural parameters of the CN_2 group are very close to those found for other diazoalkanes. The linear diazo group C(1)N(1)N(2) lies on the crystallographic twofold axis of the unit cell. The ability of bis[bis(diisopropylamino)phosphanyl]diazomethane to act as a chelating or reducing agent is discussed.

Tertiary phosphanes PR_3 are of great importance in phosphorus chemistry. They have been widely used as ligands in stabilizing metal complexes or as reactive species in metal mediated phosphorus chemistry. On the other hand, diazoalkanes have proved to be extremely useful in organic chemistry as precursors to carbenoid species and as 1,3-dipoles. In contrast to α-diazo-λ^5-phosphorus derivatives [1], which are well documented, the synthesis of α-diazophosphanes has only been recently reported [2,3]. Most of them were unstable at room temperature [3], and until now no X-ray diffraction studies had been reported. The instability of this class of compounds, like that of phosphane azides [4], is probably due to possible intra or intermolecular reactions of the diazo moiety with the phosphorus lone pair [5].

Table 1

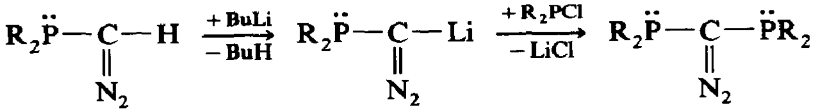
Bond lenghts (Å) and angles (°) with e.s.d.'s in parentheses

P–N(4)	1.685(4)	P–C(1)	1.845(3)	N(1)–N(2)	1.15(1)
P–N(3)	1.696(5)	C(1)–N(1)	1.28(1)	C(2)–C(4)	1.527(7)
N(3)–C(2)	1.475(6)	C(2)–C(3)	1.516(8)	C(5)–C(7)	1.524(8)
N(3)–C(5)	1.485(10)	C(5)–C(6)	1.52(1)	C(8)–C(10)	1.53(1)
N(4)–C(8)	1.480(8)	C(8)–C(9)	1.529(7)	C(11)–C(13)	1.481(15)
N(4)–C(11)	1.463(8)	C(11)–C(12)	1.504(10)		
P–C(1)–P	122.5(4)	N(2)–N(1)–C(1)	180	N(1)–C(1)–P	118.7(2)
N(3)–P–C(1)	103.2(2)	N(4)–P–N(3)	109.0(2)	N(4)–P–C(1)	101.5(2)
C(2)–N(3)–C(5)	115.5(5)	C(2)–N(3)–P	126.1(4)	C(5)–N(3)–P	118.1(3)
C(11)–N(4)–C(8)	114.9(5)	C(8)–N(4)–P	126.8(3)	C(11)–N(4)–P	117.9(4)
N(3)–C(2)–C(3)	114.7(4)	N(3)–C(1)–C(4)	111.7(5)	C(3)–C(2)–C(4)	109.3(5)
N(3)–C(5)–C(6)	113.2(5)	N(3)–C(5)–C(7)	111.4(6)	C(6)–C(5)–C(7)	111.0(5)
N(4)–C(8)–C(10)	112.8(5)	N(4)–C(8)–C(9)	113.1(5)	C(9)–C(8)–C(10)	109.4(5)
N(4)–C(11)–C(13)	113.2(7)	N(4)–C(11)–C(12)	112.7(6)	C(12)–C(11)–C(13)	110.4(8)



It was of interest to determine the X-ray structure of such a species and we report here the synthesis and crystal structure of bis[bis(diisopropylamino)phosphanyl]diazomethane **2**.

Diazophosphane **2** was synthesized in a two-step one-pot reaction by treatment of the lithium salt of bis(diisopropylamino)phosphanyldiazomethane [2], prepared from diazo derivative **1** and BuLi, with bis(diisopropylamino)chlorophosphane.



(**1**) (**2**)

(R = (i-Pr)$_2$N)

Compound **2** was recrystallized in 85% yield from an acetonitrile/benzene mixture at room temperature as air-stable orange parallelepiped crystals suitable for X-ray diffraction study. Bond lengths and angles are in Table 1. $[(i\text{-}Pr_2N)_2P]_2CN_2$ crystallizes as discrete molecules possessing a crystallographically imposed twofold axis of symmetry. The atom-labeling scheme for **2** is given in the ORTEP view of the molecule (Fig. 1). Bond parameters for the bis(diisopropylamino)phosphanyl groups are in the expected range. The value of angles around C(1) indicates sp^2

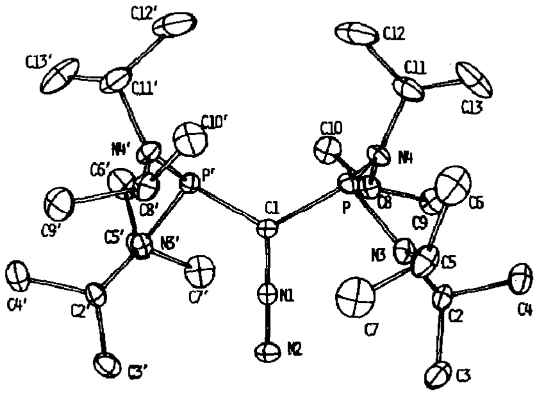


Fig. 1. ORTEP drawing of $[(i\text{-}Pr_2N)_2P]_2CN_2$. The ellipsoids correspond to 50% probability. H atoms are omitted for clarity.

hybridization. The P, C(1), N(1), N(2) atoms lie in the same plane and the linear C(1)N(1)N(2) group lies on the twofold axis. The C(1)–N(1)(1.28(1)) and N(1)–N(2)(1.15(1)) bond lengths are in the range of those usually observed for diazoalkanes, namely 1.28–1.32 and 1.12–1.15 Å, respectively. The phosphorus–carbon bond length is consistent with a P–C single bond. From consideration of valence shell electron pair repulsion, the PCP′ angle should be smaller than 120°, whereas it is unambiguously larger, namely 122.5(4)°. This may be the result of a lattice effect or more probably of a steric effect of the phosphanes. In order to check a third possibility, the presence of an intramolecular repulsion of the lone pairs of the two phosphorus atoms, we calculated their respective position and direction. The space group indicates that the two pairs exchange through a rotation of 180° around the C(1)N(1)N(2) axis. We have drawn the ORTEP diagram in which, for clarity, each electron pair is represented as an extra atom with the characteristics of a nitrogen atom, which means a tetrahedral geometry around each phosphorus and an imposed P–N distance of 1.69 Å. It is apparent from Fig. 2 that in order to decrease their interaction, the lone pairs are not located in the PCP′ plane but lie in two parallel planes which make an angle of 51.8(4)° with the PCP′ plane. Thus the value of the PCP′ angle may be reasonably attributed to the repulsion between the phosphorus lone pairs.

These crystallographic data and the IR vibration $\nu(CN_2)$ at 2010 cm^{-1}, which is in the range observed for all diazo derivatives (2100–1950 cm^{-1}), seem to indicate that there is almost no interaction between the phosphorus lone pairs and the diazo moiety.

Compound **2** should be an interesting ligand for transition metal chemistry. It might act as a monodentate ligand via the phosphorus lone pairs, via the terminal nitrogen of the diazo group, or even via electrons of the diazo moiety. In principle, it could also act as a bidentate ligand through the electron pairs of the two phosphorus atoms but, this is virtually impossible in the ground state because of the distance between and orientation of these electron pairs. On the other hand, in the excited state, **2** readily loss N_2 to give the corresponding carbene.

Experimental

All experiments were performed under dry argon or nitrogen. Melting points were uncorrected. ^1H NMR spectra were recorded on a Bruker WM250 spectrometer, and the chemical shifts are in ppm relative to external Me_4Si. ^{31}P NMR spectra were obtained on a Bruker AC80 spectrometer at 32.43 MHz. Downfield shifts are shown with a positive sign, and are in ppm relative to external 85% H_3PO_4.

Synthesis of bis[bis(diisopropylamino)phosphanyl]diazomethane (2). To the lithium salt of bis(diisopropylamino)phosphanyldiazomethane, obtained by addition of BuLi (7 mmol) to a THF solution of **1** (2 g, 7 mmol) at −78°C, was added dropwise a THF solution (30 ml) of bis(diisopropylamino)chlorophosphane (1.8 g, 7 mmol). After filtration and evaporation of the solvent, the orange residue was recrystallized from acetonitrile/benzene to give compound **2** (3.0 g, 85% yield) as orange crystals. m.p. 70–80°C (dec.); ^{31}P NMR (C_6D_6) + 65.2 ppm; ^1H NMR (C_6D_6) δ 1.10 (d, J(HH) 7 Hz, 24H, CH_3), 1.15 (d, J(HH) 7 Hz, 24H, CH_3), 3.25 (m, 8H, CH); mass spectrum, m/e 502 (M^+), 474 ($M - N_2$); Anal. Found: C, 59.70; H, 11.23; N, 16.69. $C_{25}H_{56}N_6P_2$ calcd.: C, 59.73; H, 11.23; N, 16.72%.

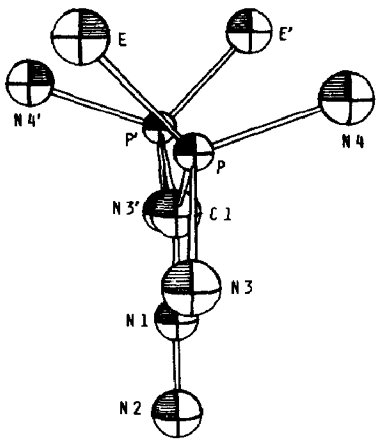


Fig. 2. ORTEP drawing showing the space location of the phosphorus lone pairs (N4 and N4′).

Structural data and crystallographic determination. Orange parallelepiped crystals of **2** were obtained from acetonitrile/benzene. The reflections were collected on an Enraf–Nonius CAD4 diffractometer, using a graphite-monochromated Mo-K_α radiation. The cell parameters were determined from a least-squares fitting of 25 centered reflections with 2θ between 17 and 30°. The space group determination showed the systematic absences (hkl with $h+k$ odd, $h0l$ with l odd) identified in full data set. A summary of crystal and intensity collection data is given in Table 2. Successful refinement was carried out in the centrosymetric space group. 2813 independent reflections, 1275 with $I > 3\sigma(I)$ were measured using $\theta/2\theta$ scans for

Table 2

Crystal data and details of data collection and structure refinement for $[(i\text{-}Pr_2N)_2P]_2C(N_2)$

Formula	$P_2N_6C_{25}H_{56}$
fw, g	502.70
Cryst. system	Monoclinic
Space group	$C2/c$
a, Å	12.044(2)
b, Å	28.661(4)
c, Å	10.301(1)
β, °	116.13(1)
V, Å^3	3192(2)
Z	4
d_{calc}, g/cm^3	1.045
μ(Mo-K_α), cm^{-1}	1.24
Temperature, °C	20±2
Scan method	$\theta/2\theta$
Data collcn range (θ), deg	$1 < 2\theta < 50$
Take off angle, deg	1.75
no. of reflections measured	2813
no. of unique data with $(I) > 3\sigma(I)$	1275
no. of parameters refined	151
R^a	0.0520
$R_w{}^b$	0.0526

[a] $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 3

Fractional atomic coordinates with e.s.d.'s in parentheses

Atom	x/a	y/b	z/c
P	0.36054(12)	0.11627(5)	0.73497(14)
C(1)	1/2	0.1472(2)	3/4
N(1)	1/2	0.1918(2)	3/4
N(2)	1/2	0.2318(2)	3/4
N(3)	0.2694(4)	0.1600(2)	0.7441(4)
C(2)	0.1969(5)	0.1927(2)	0.6268(6)
C(3)	0.2101(6)	0.2436(2)	0.6717(7)
C(4)	0.0600(5)	0.1797(2)	0.5538(7)
C(5)	0.2479(6)	0.1631(2)	0.8752(7)
C(6)	0.2107(6)	0.1169(3)	0.9165(7)
C(7)	0.3593(7)	0.1839(3)	1.0022(7)
N(4)	0.3017(4)	0.0962(1)	0.5639(4)
C(8)	0.3113(5)	0.1186(2)	0.4397(5)
C(9)	0.1855(5)	0.1291(2)	0.3138(6)
C(10)	0.3895(6)	0.0903(2)	0.3846(6)
C(11)	0.2477(7)	0.0494(2)	0.5354(8)
C(12)	0.3412(9)	0.0119(2)	0.6113(9)
C(13)	0.1399(8)	0.0447(3)	0.5676(11)

2θ from 1 to 50°. Intensities of three reflections measured every 2 h during data collection varied less than 2.5%. The data were corrected for Lorentz polarization, and absorption effects. The structure was solved with MULTAN, with refinement by full-matrix least-squares based on $|F_o|$. The SHELX package was used [6]. After an anisotropic refinement for all non-H atoms, the hydrogen atoms were fixed at idealized positions (C–H 0.96 Å, U 0.09 Å kept fixed) and repositioned after each least-squares cycle. Final parameters are $R = 0.0520$, $R_w = 0.0526$ [7*] and $S = 2.17$ for 151 variables, with shift mean 0.01σ, max. 0.05σ in final cycle. The largest residual electron density on final ΔF map was equal to 0.2 eÅ^{-3}. The scattering factors were taken from ref. 8 for P, N, and C and from ref. 9 for H.

The final fractional atomic coordinates are listed in Table 3. Lists of temperature factors, calculated hydrogen coordinates and structure factors are available from the authors.

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* Reference number with asterisk indicates a note in the list of references.