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1,3-Diphenyl-2,2,2,4,4,4-hexazido-1,3-diaza-2,4-diphosphetidine: synthesis and structural characterisation of the first nitrogen-penta-coordinated phosphorus with three azide-groups†

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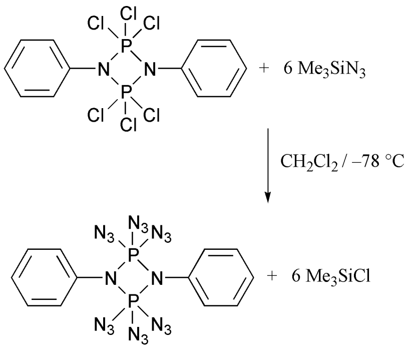
$(C_6H_5)_2N_2P_2(N_3)_6$ 1 has been prepared and characterised by multinuclear NMR, vibrational spectroscopy and single crystal X-ray analysis; the normal modes of 1 have been calculated and the antisymmetric stretching vibration of the azide group has been discussed.

In 1970 Horn reported on the reaction of 1,3-dimethyl-2,2,2,4,4,4-hexachloro-1,3-diaza-2,4-diphosphetidine with NaN_3 in MeCN yielding a highly explosive compound which was only poorly characterised.[1] To our knowledge only a few crystal structures of mono- and di-substituted phosphorus azides[2] and nitrogen-penta-coordinated phosphorus compounds[2c,3] have been published. Here we report on the synthesis and structural characterisation of the first nitrogen-penta-coordinated phosphorus species substituted with three azide groups, which can be considered as a hexazidodiphosphadiazacyclobutane.

1,3-Diphenyl-2,2,2,4,4,4-hexazido-1,3-diaza-2,4-diphosphetidine **1** was obtained in high yield as a colourless solid from the reaction of 1,3-diphenyl-2,2,2,4,4,4-hexachloro-1,3-diaza-2,4-diphosphetidine with trimethylsilyl azide in CH_2Cl_2 solution, [eqn. (1)].



(1)

1

Single crystals suitable for X-ray diffraction determination§ were grown from CH_2Cl_2. A view of the molecular structure of **1** is shown in Fig. 1. Compound **1** crystallises in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The two crystallographically different molecules display nearly identical bond lengths and angles.

The molecular structure of **1** reveals C_i symmetry in which each phosphorus is coordinated by five nitrogen atoms. The coordination sphere around the phosphorus atom can be regarded as a slightly distorted trigonal bipyramid.

The N_2P_2 ring is planar with a P–N–P angle of 100.6(2)° and a N–P–N angle of 79.4(2)°. The azide groups are slightly bent with N–N–N angles ranging from 171.1(4) to 175.1(4)° which are in accordance with the structures of other covalent phosphorus azides.[2]

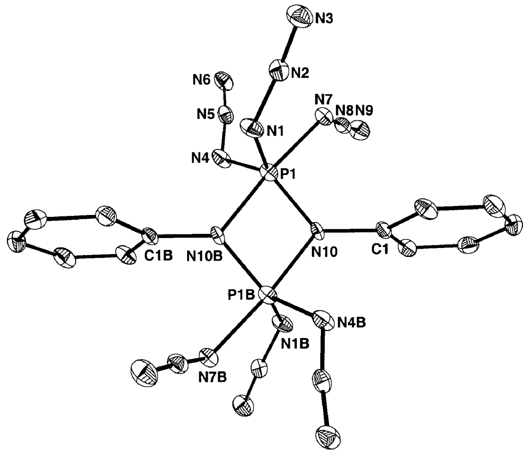


Fig. 1 An ORTEP plot of the molecular structure of compound **1** with thermal ellipsoids at 25% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.703(3), P(1)–N(4) 1.713(3), P(1)–N(7) 1.804(3), N(1)–N(2) 1.252(4), N(4)–N(5) 1.253(4), N(7)–N(8) 1.240(4), N(2)–N(3) 1.118(4), N(5)–N(6) 1.118(4), N(8)–N(9) 1.130(4), P(1)–N(10) 1.643(4), N(10)–P(1B) 1.774(3); P(1)–N(10)–P(1B) 100.6(2), N(10)–P(1)–N10(B) 79.4(2).

Since the two nitrogen ring atoms occupy different positions in the coordination sphere around the phosphorus atom [N(10) equatorial, N(10B) axial position, with respect to P(1) and *vice versa* for P(1B)] two considerably different $P–N_{ring}$ bond lengths [1.643(4) and 1.774(3) Å] are observed which are similar to the bond lengths found in $Me_2N_2P_2Cl_6$.[4] A similar large difference in the P–N bond length is found for the azide groups [1.703(3), 1.713(3) and 1.804(3) Å] as each phosphorus atom in **1** is surrounded by two equatorial [eq, N(1), N(4)] and one axial [ax, N(7)] azide groups. NBO analysis indicates that this structural feature can be rationalised by a 'weaker' two-electron–three-centre bond unit along the N(10B)–P(1)–N(7) [and N(10)–P(1B)–N(7B)] axis whereas the equatorial positions can be best described by two-electron–two-centre bond units.† This rather special bonding situation can best be understood in the picture of localised bond orbitals (NBOs) by strong non-covalent contributions between the two monomeric units.[5] The one lone pair (p-type atomic orbital) on each $N(Ph)P(N_3)_3$ unit interacts with the antibonding σ $P–N_3$ bond system of the second monomeric unit and *vice versa* (Fig. 2). There are three strong intramolecular donor–acceptor interactions of this type which weaken the $P–N_3$ bonds (especially $P–N_{3,ax}$) and account for the rather long $P–N_3$ bonds. However, since the lone pair (LP) on the ring nitrogen atom lies in-plane with the $P–N_{3,ax}$ bond of the second monomeric unit, the interaction with the unoccupied, antibonding $\sigma^*(P–N_{3,ax})$ is stronger than the interaction with the 'out-of-plane' $\sigma^*(P–N_{3,eq})$ bond orbitals [$LP(N_{ring}) \rightarrow \sigma^*(P–N_{3,ax})$: 85, $LP(N_{ring}) \rightarrow \sigma^*(P–N_{3,eq1})$: 38, $LP(N_{ring}) \rightarrow \sigma^*(P–N_{3,eq2})$: 34 kcal mol^{-1}].† This

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† Electronic supplementary information (ESI) available: experimental details for **1**, Fig. SI 1 and computational details. See http://www.rsc.org/suppdata/cc/b0/b006944m/

‡ For queries relating to crystal structure analysis.

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Table 1 Selected IR and Raman data for **1**

Calc. IR / Raman[a]	Exp. IR / Raman[b]	Symmetry	Approximate assignment[c]	Displacement vector[d] N(4)	N(1)	N(7)
2164 (0; 472)	2158 (0; 7)	A_g	ν_{as}, i. p., $N_{3,eq}$	↓ N ↑ N	↓ N ↑ N	N N
2158 (840; 0)	2154 (s; 0)	A_u	ν_{as}, o. p., $N_{3,eq}$	↓ N ↑ N	↓ N ↑ N	N N
2143 (1804; 0)	2142 (s; 0)	A_u	ν_{as}, o. p., $N_{3,eq}$	↑ N ↓ N	↓ N ↑ N	N N
2142 (0; 176)	2136 (0; 4)	A_g	ν_{as}, i. p., $N_{3,eq}$	↑ N ↓ N	↓ N ↑ N	N N
2105 (0; 250)	2111 (0; 1)	A_g	ν_{as}, i. p., $N_{3,ax}$	N N	N N	↓ N ↑ N
2102 (1918; 0)	2113 (m; 0)	A_u	ν_{as}, o. p., $N_{3,ax}$	N N	N N	↓ N ↑ N

[a] Wavenumbers in cm^{-1}; calculated IR intensities (km mol^{-1}) and Raman activities ($Å^4$ AMU^{-1}) in parenthesis; HF/6-31G(d,p) calculated wavenumbers scaled with $f = 0.8317$; *cf.* B3LYP/6-31G(d,p) unscaled frequencies (symmetry, IR intensity in km mol^{-1}): 2302 (A_g, 0), 2293 (A_u, 557), 2287 (A_u, 1909); 2287 (A_g, 0); 2270 (A_g, 0) and 2272 (A_u, 943) cm^{-1}. [b] Relative IR and Raman intensities in parenthesis. [c] $N_{eq}(1)$ equivalent to $N_{eq}(1B)$, $N_{eq}(4)$ equivalent to $N_{eq}(4B)$, $N_{ax}(7)$ equivalent to $N_{ax}(7B)$. i. p. = In phase: according to C_i-symmetry all equivalent N_3-groups vibrate in phase; o. p. = out of phase: according to C_i-symmetry the movement of all equivalent N_3-groups is shifted by 180°. [d] These displacement vectors represent approximations. Weak coupling between the axial and the equatorial azide groups is neglected for clarity.

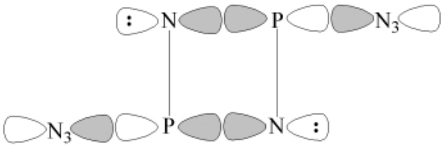

Fig. 2 Intramolecular donor–acceptor interaction in **1**: $LP(N_{ring}) \rightarrow \sigma^*(P–N_3)$.

strong interaction of the nitrogen lone pair with the σ* $P–N_3$ bonds can be considered as the main driving force of the cyclisation. Moreover, this donor–acceptor bonding is strengthened by the donor properties of the phenyl ring and accounts for the stability of the dimer. Previous NMR studies on phosphineimine/diazadiphosphetidine equilibria have shown that the formation of the dimer strongly depends on the donor properties of the nitrogen substituents.[6] Weaker donor substituents (*e.g.* $C_6H_2Cl_3$-2,4,6) result in equilibria between the monomeric and dimeric species.

As a result of this intriguing bond situation, the axial $P–N_3$ bond displays a higher ionic character which is manifested by a better π delocalisation along the azide unit leading to a longer terminal N(8)–N(9) bond length and a shorter N(7)–N(8) bond length than in the equatorial azide groups with a less polar $P–N_3$ bond (Fig. 1). In agreement with this, the hybridisation on the nitrogen attached to the P atom increases from $N_{ax}(7)$ ($sp^{1.01}$) < $N_{eq}(1)$ ($sp^{1.23}$) < $N_{eq}(4)$ ($sp^{1.31}$) resulting in a larger N(7)–N(8)–N(9) angle compared to the N(4)–N(5)–N(6) and N(1)–N(2)–N(3) angles.

Since the terminal N(8)–N(9) bond length of the axial azide group is significantly longer, the antisymmetric stretching vibrations of the axial azide group appear at lower wavenumbers than the antisymmetric stretching vibration of the equatorial azide groups (Table 1). The calculated, scaled antisymmetric stretching frequencies are in excellent agreement with the experimentally observed vibrational frequencies and confirm the results of the NBO analysis.† Owing to C_i symmetry of the molecule, there are six normal modes describing the antisymmetric stretching vibration of the N_3 moiety which are either Raman active (3 A_g) or IR active (3 A_u). In agreement with C_i symmetry, the Raman and the IR spectra of solid **1** show each three absorbtions: Raman (2158, 2135, 2111 cm^{-1}); IR (2154, 2142, 2113 cm^{-1}), which are in the typical region for the antisymmetric stretching vibration of azides.[7] The approximate displacement vectors and assignments are given in Table 1.

The difference between the axial and equatorial azide groups was also observed in the ^{14}N NMR spectrum of **1**. The ^{14}N NMR spectrum of a covalently bonded azide group (connectivity $X–N_\alpha–N_\beta–N_\gamma$) usually shows three resonances whereas the signal of the N_α and N_γ are very broad owing to the large quadrupole moment of ^{14}N. The ^{14}N NMR spectrum of **1** reveals three signals for the N_β atoms at −152 (br, sh) and −154 ppm which can be assigned to the two N_{eq} and N_{ax}. The resonances of the N_γ atoms are found in the region of −166 (br, N_{eq}) and −169 (N_{ax}) ppm.[8] A single resonance was observed in the ^{31}P NMR spectrum at −87.6 ppm, in the region typical for penta-coordinated phosphorus.

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Notes and references

§ *Crystal data*: $C_{12}H_{10}N_{20}P_2$ **1**: $M = 496.34$, triclinic, space group $P\bar{1}$, $a = 7.342(2)$, $b = 8.551(2)$, $c = 17.879(4)$ Å, $\alpha = 88.527(3)$, $\beta = 85.499(4)$, $\gamma = 67.684(3)°$, $V = 1035.1(4)$ $Å^3$, $Z = 2$, μ(Mo-Kα) = 0.262 mm^{-1}, $\lambda = 0.71073$ Å, $T = 193$ K, 5983 reflections measured, 3153 unique ($R_{int} = 0.0408$) which were used in all calculations. Final R indices [$F > 4\sigma(F)$], $R1 = 0.0488$, $wR2 = 0.1148$. The structure was solved using direct methods and refined by full-matrix least squares on F^2 using SHELXL-97. Data for compound **1** were collected on a Siemens CCD Area detector using Mo-Kα radiation. CCDC 182/1843. See http://www.rsc.org/suppdata/cc/b0/b006944m/ for crystallographic files in .cif format.

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