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Tetrahedron
Tetrahedron 63 (2007) 9129–9133

The structural and theoretical study of 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole in the solid state

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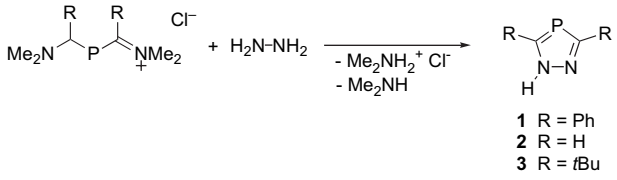
Received 17 May 2007; revised 19 June 2007; accepted 21 June 2007
Available online 27 June 2007

Abstract—The *N*-, *P*-containing five-membered heterocyclic compound 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole (**1**) was prepared in good yield and has been structurally characterized. 1*H*-3,5-Di-phenyl-1,2,4-diazaphosphole (**1**), crystallizing in two unexpected cyclic dimers with N–H···N hydrogen bonds, presents in the solid state a dynamic proton disorder implying a dynamic equilibrium within both dimers. The conformations of the phenyl rings, the disorder of the NH protons, and the intermolecular hydrogen bond of several 1,2,4-diazaphospholes (**1**–**5**) in the solid state have been rationalized by DFT [B3LYP/6-311++G(d,p)] calculations.

1. Introduction

The nitrogen- and phosphorus-containing five-membered heterocycles prepared by the reaction of 1,3-bis(dimethylamino)-2-phosphaallyl chlorides and hydrazine in chloroform were formulated as 1*H*-1,2,4-diazaphospholes (**1**–**3**) on the basis of spectroscopic studies (Scheme 1).[1]



Scheme 1. 1*H*-3,5-Di-substituted-1,2,4-diazaphospholes **1**–**3**.

Subsequent work showed that, in the solid state, the structures of 1*H*-1,2,4-diazaphophole (**2**) and 1*H*-3,5-di-*tert*-butyl-1,2,4-diazaphosphole (**3**) crystallize in a helix of order 3 and a dimer, respectively, in which significant intermolecular disorder NH-hydrogen bonds were revealed.[2] The structure of 5-diisopropylamino-3-trifluormethyl-1*H*-1,2,4-diazaphosphole (**4**) is also known, but further information about the motif of intermolecular NH-hydrogen bond was not reported in the published paper.[3] From a molecular point of view, 1*H*-1,2,4-diazaphospholes can be considered 4-phosphapyrazoles; thus, their conformations in the solid state may be compared to those of the corresponding pyrazoles. Indeed, for **2** and **3**, this is the case, and the conformations are similar to those of 1*H*-pyrazole[4] and 1*H*-3,5-di-*tert*-butyl-pyrazole, respectively.[5] While 1*H*-3,5-di-phenyl-pyrazole features a cyclic tetramer with N–H···N hydrogen bonds,[6] the solid state structure of 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole (**1**) has not yet been solved owing to the difficulty in obtaining crystals for X-ray diffraction analysis. Such problem presumably stems from an extraordinary arrangement of the molecules in the crystal lattice. Recently, some of us investigated the dynamic properties of **1** by solid state ^{13}C and ^{15}N CPMAS NMR spectra as well as by an approach to GIAO/ab initio calculations.[7] The results indicated a probable oligomeric aggregate of **1** with a dynamic behavior of intermolecular solid state proton transfer (ISSPT). 1*H*-3,5-Di-phenyl-1,2,4-diazaphosphole (**1**) has attracted much interest as a potential candidate in coordination chemistry,[8] in accurate electron density studies,[8] as well as for analysis of the solid state properties of these heterocycles.[7] As a first step, we have now optimized the preparation of this compound, determined its crystal structure to confirm its molecular constitution, and carried out a theoretical analysis using B3LYP/6-311++G(d,p) calculations[9,10] to understand the origin of the proton disorder present in the solid state structure.

Keywords: Azaphospholes; Ab initio calculations; 1*H*-1,2,4-Diazaphospholes; Hydrogen bonding; X-ray.
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doi:10.1016/j.tet.2007.06.069

2. Results and discussion

2.1. Synthesis of compound 1 (Scheme 1)

Previously, Schmidpeter and Willhalm reported that the reaction of 1,3-bis(dimethylamino)-2-phosphaallyl chlorides and hydrazine led to formation of 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole (**1**). This compound could be isolated in mild yield following extraction with ether.[1] In the course of an investigation on 3,5-di-phenyl-1,2,4-diazaphospholide metal complexes,[8] we found that the yield of **1** was significantly improved by addition of excess of hydrazine in the reaction system, which could be washed off with water from the combined extracting solvent phase (diethyl ether). The resulting residue, after removal of ether, was sublimed at about 200 °C in high vacuum (0.01 mmHg) affording **1** as white pure solid in 85% yield. Notably, **1** should be kept in dark due to the light sensitivity otherwise it will decompose into a yellowish solid within few days.

2.2. Structural characterization of compound 1

The colorless crystals of **1** were obtained by a method of solid phase recrystallization in high vacuum at 200 °C by using a Büchi Glass Oven (B-585) apparatus. The structure was solved with SHELXS-97[11] and refined by full-matrix least-squares analysis with SHELXL-97[12] using 5220 independent reflections (θ_{max}=27°) with $I>2\sigma(I)$. The results of the analysis confirm formula **1**.

Compound **1** crystallizes in the monoclinic space group $P2_1/c$. Molecular dimensions are shown in Figures 1 and 2. As illustrated in these figures, and concerning the conformation of the phenyl rings attached to the heterocycle, the average planes formed by the phenyl groups and the heterocycle ring show that they are not coplanar (see Section 4, Table 1). Due to the difference in average phenyl dihedral angles, there are two molecular conformations [A (N1, N2) and B (N3, N4)] present in the crystal in a ratio of 1:1. Being the average phenyl dihedrals 26.88(18)° for the conformation A and 23.95(20)° for B, the total average phenyl dihedral of the molecules A and B is 25.42(19)° [(26.88(18)+23.95(20))/2=25.42(19)°]. However, given only single set of the signals in the spectrum, the solid state ^{13}C CPMAS NMR spectroscopic data for **1** seem to suggest a dynamic process between A and B at room temperature, in agreement with those observed by some of us previously.[7] Notably, intermolecular hydrogen bonds in the solid state with disordered NH protons involving nitrogen atoms are found, evidenced by the broad signal in the solid state ^{15}N CPMAS NMR spectrum as well as the almost identical internal angles at nitrogen atoms (vide infra). More interesting, however, is the presence of the intermolecular hydrogen bonds only between the nitrogen atoms of two molecules with an identical conformation (A–A or B–B) (Fig. 2). Since the nitrogen atoms in the molecules are excellent hydrogen bonding formers, the discrete molecules are linked into two different cyclic dimers by the intermolecular hydrogen bonding interactions [N(1)–H(1)···N(2A) 2.884(2) Å; N(2)–H(1A)···N(1A) 2.884(2) Å] (symmetry codes: [−*x*+1, −*y*+1, *z*]), and [N(3)–H(3)···N(4A) 2.890(2) Å; N(4)–H(3A)···N(3A) 2.890(2) Å] (symmetry codes: [−*x*, −*y*+1, −*z*]). The conformation of **1** is therefore in contrast to that of the tetrameric 1*H*-3,5-di-phenyl-pyrazole.[6] Additionally, the heterocyclic rings for A and B in **1** are almost planar with mean deviations 0.0011 Å and 0.0032 Å from the ring plane. There are no significant interactions among adjacent dimers. The bond lengths of N(1)–N(2) (1.341(2) Å), P(1)–C(1) (1.7404(18) Å) in the dimer A–A and N(3)–N(4) (1.344(2) Å), P(2)–C(15) (1.7393(18) Å) in the dimer B–B are slightly longer than those found in 1*H*-1,2,4-diazaphosphole (N–N 1.323(3) Å, P–C 1.710(3) Å).[2] The angles of C–P–C [C(1)–P(1)–C(2) 87.01(9)° in A, C(15)–P(2)–C(16) 87.30(9)° in B] are comparable to those found in 1*H*-3,5-di-*tert*-butyl-1,2,4-diazaphosphole (C–P–C 87.3(2)°).[2] The internal angles at nitrogen atoms of the heterocyclic ring are slightly different for the molecule A (N1 114.09(19)° vs N2 113.11(19)°) and for the molecule B (N3 114.11(18)° vs N4 112.99(17))°, clearly implying the dynamic proton disorder on both nitrogen atoms even though the proton is somewhat closer to one of the two nitrogen atoms (N1 and N3).

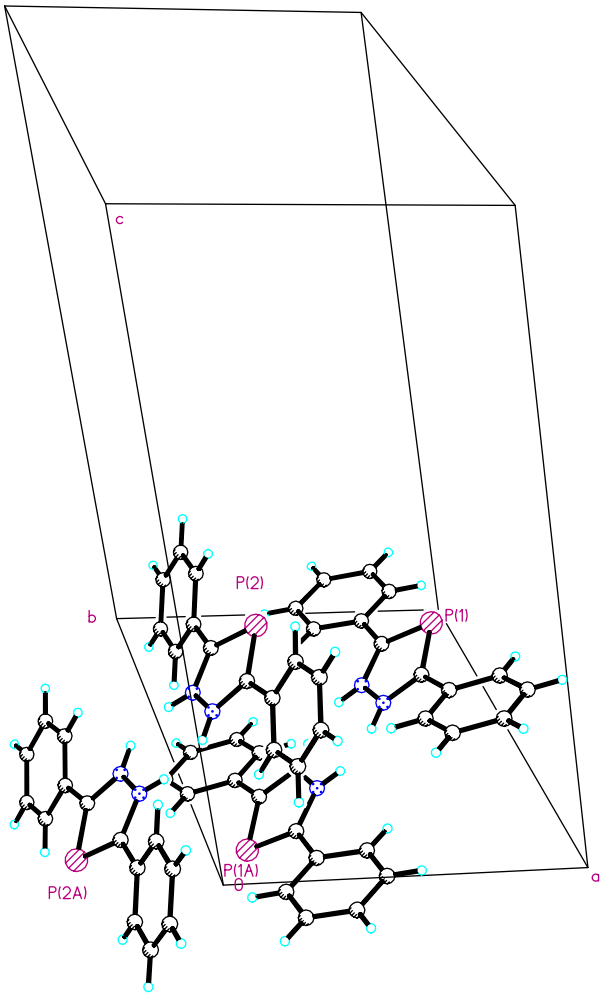


Figure 1. A stereoview of part of the crystal structure of 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole.

Table 1. Selected torsion angles [°] of **1**

C(4)–C(1)–C(3)–P(1)	27.5 (2)
P(1)–C(2)–C(9)–C(10)	26.25 (15)
P(2)–C(15)–C(17)–C(18)	21.7 (2)
C(28)–C(16)–C(23)–P(2)	26.2 (2)

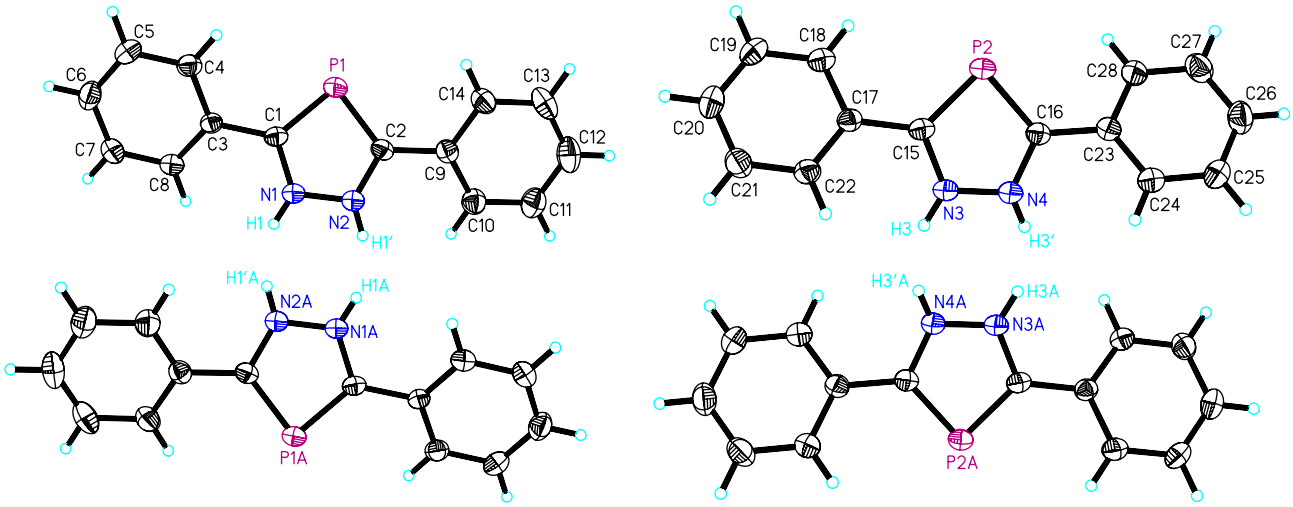


Figure 2. An ORTEP plot of two dimeric 1*H*-3,5-di-phenyl-1,2,4-diazaphospholes showing displacement ellipsoids at 50% probability level.

2.3. Computational studies

To gain a better understanding of the conformation of the phenyl rings in **1**, the disorder of the NH protons and the intermolecular hydrogen bond of 1*H*-1,2,4-diazaphospholes in the solid state, we have performed a series of B3LYP/6-311++G(d,p) calculations of compounds **1**–**5** (Scheme 2).

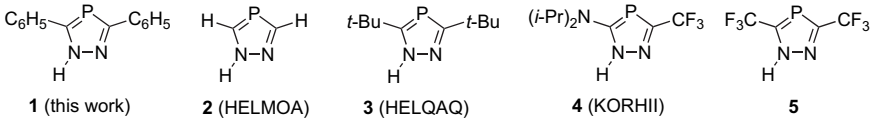
Previously, some of us published the results of B3LYP/6-31G* calculations on compounds **3** and **5**.[7] Table 2 shows the results obtained at the B3LYP/6-311++G(d,p) level on compounds **1**–**5**, the last one being unknown.

It is clear that in the case of **4** the NH proton is localized while in the cases of **1**, **2** and **3**, the proton is delocalized between both nitrogen atoms in a 50:50 disorder. In the case of **4**, the other tautomer (5-diisopropylamino-3-trifluormethyl-1*H*-1,2,4-diazaphosphole) is expected to be much less stable since in pyrazoles and in 1*H*-1,2,4-triazoles the CF_3 group 'prefers' the 3-position,[15,16] and for this reason there is no disorder. The difference, on the basis of the solid state NMR results,[7] is that the disorder is static in the case of **2** (helical chain) and **3** (cyclic dimer) while it is dynamic in the case of **1** (two cyclic dimers).

The phenyl groups in the analogous case of 1*H*-3,5-disubstituted pyrazoles, are almost coplanar for the 3-phenyl because the attractive interaction between an aromatic CH and the pyridinic nitrogen lone pair while they are twisted in the case of 5-phenyl group due to a repulsive interaction between the CH and the NH.[17] In the case of **1**, the twisted conformations of the phenyl groups are obviously caused by an intramolecular interaction of adjacent groups in the similar manner. On the basis of the solid state NMR results,[7] it is clear that a dynamic equilibrium is present between the two dimers of **1**. The calculated total average dihedral angle is consistent with that found from the crystallographic data (Scheme 3).

3. Conclusion

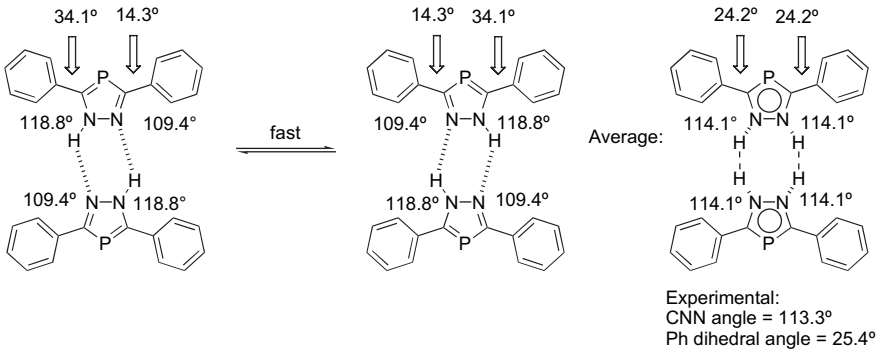
In summary, the chemists' interest in compound **1** arises from the very unusual existence of two different cyclic dimers linked by intermolecular disordered hydrogen bonds, including a dynamic equilibrium in the solid state. Such conformations in solid state are unprecedented in the structures of five-membered heterocycles. A theoretical study of several 1*H*-1,2,4-diazaphospholes using the DFT [B3LYP/6-311++G(d,p)] calculations promoted the understanding of the observed structural features as to the twisted conformation of the phenyl rings of **1**, the disorder of the NH protons and the intermolecular hydrogen bonds. It is now clear that three 1*H*-1,2,4-diazaphospholes with identical substituents at positions 3 and 5, Ph **1**, H **2** and *t*-Bu **3**, crystallize in three



Scheme 2. The 1*H*-1,2,4-diazaphospholes studied.

Table 2. Calculated and experimental geometries of compounds **1**–**5** (angles in deg)

Compd	$CN(H)N_{calcd}$	$CNN(H)_{calcd}$	Average	Refcode[13]	$CN(H)N_{exp}$	$CNN(H)_{exp}$
1	109.4	118.8	114.10	This work	114.2	114.3
1				This work	112.3	112.5
2	108.2	117.9	113.05	HELMOA[14]	112.2	112.3
3	109.5	119.0	114.25	HELQAQ	113.3	113.4
4	108.3	118.8	[113.35]	KORHII	107.7	117.7
5	108.5	117.5	113.00	—		



Scheme 3. The dynamic situation present in compound **1**.

different structures: two dimers with ISSPT, helix (no ISSPT) and dimer (no ISSPT), respectively. The relationship between nature of 1*H*-3,5-substituted pyrazoles and the hydrogen bond pattern present in the crystal was recently reported;[18,19] however, the corresponding structural studies of 1*H*-1,2,4-diazaphospholes are still at the initial stages. Thus, these compounds deserve further structural investigations using X-ray crystallography, solid state ^{13}C and ^{15}N CPMAS NMR (^{15}N labeled) and theoretical calculations.[20]

4. Experimental section

4.1. General experimental procedures

The starting materials *N*,*N*-dimethylbenzamide (98%) and oxalyl chloride (98%) were commercially available from Acros, tris(trimethylsilyl)phosphine (95%) from Aldrich, hydrazine from SCR, and used without further purification. All preparations were performed under an atmosphere of dry N_2-free O_2, employing either Schlenk-line techniques or an inert-atmosphere vacuum glovebox. Solvents were dried according to standard methods. Access to the required 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole (**1**) was achieved by an optimized method referring to the literature.[1] Melting points were taken on a hot-plate microscope apparatus and were uncorrected. The single crystals were prepared by the solid phase recrystallization on a Büchi Glass Oven (B-585). ^1H NMR spectra were recorded with a Bruker AV-500 spectrometer (500 MHz for ^1H NMR). Chemical shifts are reported as parts per million (ppm) in δ units on the scale downfield from tetramethylsilane (TMS). X-ray data were collected on a Bruker Smart APEX-2 diffractometer.

Table 3. Bond lengths [Å] and angles [°] of **1**

P(1)–C(1)	1.7404 (18)	C(1)–N(1)–N(2)	114.09 (19)
N(1)–C(1)	1.329 (2)	C(2)–N(2)–N(1)	113.11 (19)
N(1)–N(2)	1.341 (2)	C(15)–N(3)–N(4)	114.11 (18)
P(2)–C(15)	1.7393 (18)	N(1)–C(1)–C(3)	118.95 (17)
N(3)–C(15)	1.336 (2)	N(1)–C(1)–P(1)	112.73 (15)
N(3)–N(4)	1.344 (2)	N(2)–C(2)–C(9)	119.03 (17)

4.2. Synthesis of 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole (1)

To a solution of 1,3-bis(dimethylamino)-2-phosphaallyl chlorides (50 mmol) in chloroform (150 mL),[1] hydrazine (55 mmol) was added slowly. After stirred for 18 h at room temperature, the solution was refluxed until the brown-red color disappeared. The volatile components were then removed under reduced pressure, and the resulting residue was extracted with ether (5×20 mL). The combined organic phase was washed with water (2×10 mL) to remove the remaining hydrazine. After the removal of ether on a rotate distillation apparatus, the resulting residue was sublimed at 200 °C in high vacuum (0.01 mmHg) to afford white solid (10.12 g, 85.0%), which was kept in dark due to the light sensitivity (Mp 218–220 °C). The spectra data are identical to those reported in the literature.[1]

4.3. Crystal growth of 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole (1)

The purified 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole powder was charged into a glass tube (diameter 2 cm, 10 cm long), and then compacted. The tube was set on a Büchi Glass Oven (B-585) and heated in high vacuum (0.01 mmHg) at 200 °C for about 24 h to give monocrystals of sufficient size suitable for X-ray diffraction analysis in the solid phase of sample. During which time, a partial amount of 1*H*-3,5-di-phenyl-1,2,4-diazaphosphole was sublimed on

Table 4. Hydrogen bonds [Å and deg] of **1**

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(4)–H(3′)···N(3)#1	0.803 (19)	2.21 (3)	2.890 (2)	142 (4)
N(2)–H(1′)···N(1)#2	0.81 (4)	2.16 (4)	2.884 (2)	148 (3)
N(3)–H(3)···N(4)#1	0.84 (3)	2.19 (3)	2.890 (2)	141 (3)
N(3)–H(3)···N(3)#1	0.84 (3)	2.73 (3)	3.143 (3)	112 (2)
N(1)–H(1)···N(2)#2	0.81 (3)	2.17 (3)	2.884 (2)	146 (3)
N(1)-H(1)···N(1)#2	0.81 (3)	2.72 (3)	3.167 (3)	116 (2)

Table 5. Crystal data and structure refinement details of **1**

Crystal data	**1**
Mol. Formula	$C_{14}H_{11}N_2P$
M_r	238.22
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.5341 (13)
b/Å	14.0033 (19)
c/Å	18.473 (2)
β/°	103.342 (2)
V/Å^3	2399.7 (6)
Z	8
D_x/g cm^{-3}	1.319
Crystal size/mm	0.476×0.332×0.180
Crystal color	Colorless
μ(Mo Kα)/mm^{-1}	0.206
Total data	13,891
Unique data	5220
Observed data	2880
R_{int}	0.0607
θ_{max}/°	27.0
$R[F^2>2\sigma(F^2)]$	0.0436

the Büchi Glass Oven. However, we were unable to obtain the monocrystals of sufficient size from sublimation.

4.4. X-ray structural analysis

Data collection: SMART;[21] cell refinement: SAINT;[21] data reduction: SAINT and SHELXTL;[21] program used to solve structure: SHELXS-97;[11] program used to refine structure: SHELXL-97;[12] molecular graphics: SHELXL;[12] software used to prepare material for publication: SHELXL.[12] Crystallographic data for **1** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CCDC 630888) (Tables 3–5).

Acknowledgements

The synthesis was performed at Fudan University, Shanghai, China, and support from NSFC (Grant no. 20571017); the theoretical analysis was carried out at Instituto de Química Médica, CSIC, Madrid, Spain, and support from the Ministerio de Educación y Ciencia of Spain (Project number CTQ2006-14487-C02-01/BQU). X-ray data were collected at Shanghai Institute of Organic Chemistry, Chinese Academy of Science.

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