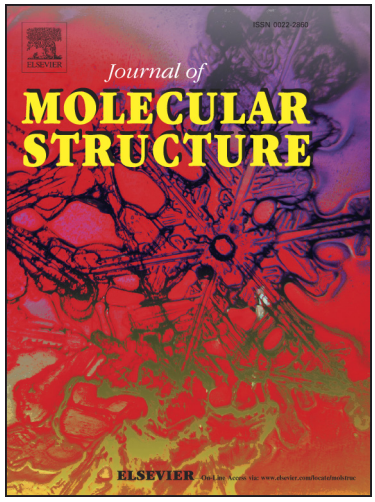

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1*H*-1,2,4-Diazaphospholes: Synthesis, Structural Chracterization, and DFT Calculation

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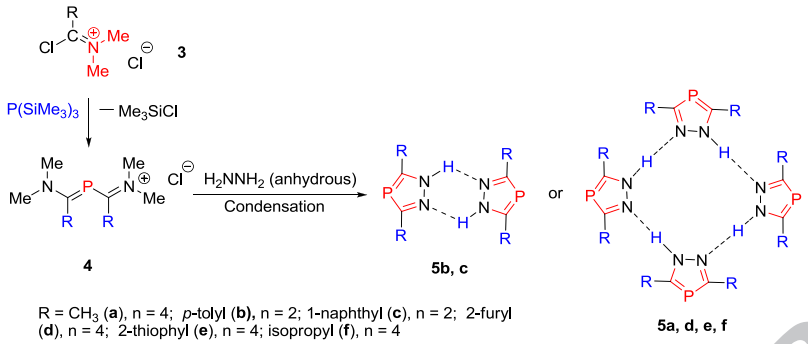
KEYWORDS: DFT calculation, 1H-1,2,4-diazaphosphole, Hydrogen bonding, Synthesis, X-ray diffraction analysis



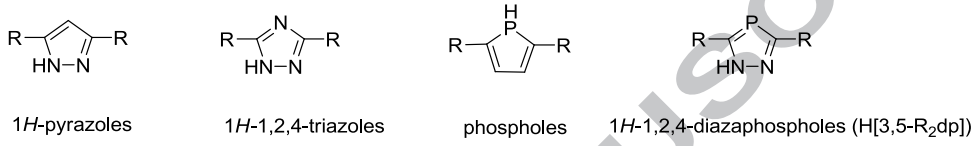
Abstract: A few 1*H*-1,2,4-diazaphospholes H[3,5-R_2dp] (R = methyl (**5a**), *p*-tolyl (**5b**), 1-naphthyl (**5c**), 2-furanyl (**5d**), 2-thienyl (**5e**), and isopropyl (**5f**)) were prepared and structurally characterized by a substantial experimental modification of the synthetic protocol. The molecules of all compounds are linked into oligomers via the bridges of NH···N hydrogen bonds in solid state. The tetrameric feature of **5a**, and **5d–f** represents a new motif of hydrogen-bonded 1*H*-1,2,4-diazaphospholes in solid state. The DFT calculation at the B3LYP/6-311++G** level suggested the possible proton disorder with intermolecular solid state proton transfer (ISSPT) between 1*H*-1,2,4-diazaphosphole rings.

1. Introduction

Heterocycles containing a low-coordinated phosphorus center[1] have found widespread applications ranging from ligand in metal complexes,[2] devices in material science[3] to fundamental importance in theoretical and experimental research.[4–7] 1*H*-1,2,4-Diazaphosphole H[3,5-R_2dp], exhibiting electrochemical and coordinating properties endowed by the low-coordinated P($\sigma^2\lambda^3$) atom, represents a class of unique aromatic five-membered heterocyclic system,[8,6] and may be viewed as a hybrid molecule of the corresponding phosphole[9] and pyrazole[10] (P-doping pyrazole),[5] or as a 1*H*-1,2,4-trizole (pyrazole) analogue in which 4-nitrogen atom (4-CH group) is replaced by a phosphorus atom ($\sigma^2\lambda^3$) (Chart 1).[7] The recent theoretical analysis has suggested that the 1*H*-1,2,4-diazaphosphole unit is a highly potential efficient electronic transfer bridge which can greatly enhance the second-order polarizability (β) values of organic molecules for obtaining good second-order nonlinear optical (NLO) properties.[11] Especially, as attested to by a few of the reports on the emerging application to complexes and catalysis as a 6π-aromatic monoanionic ligand,[12] the 1*H*-1,2,4-diazaphosphole can be even reduced to a persistent dianionic radical form,[13] of which the electronic structure disobeys 4n + 2 Hückel rule.[13] This unusual result, upon the low-coordinated phosphorus ($\sigma^2\lambda^3$) atom,[14] has attracted interest in an extensive family of persistent 1,2,4-diazaphosphole dianion radicals[13] that are potential in polymerization catalysis,[15] electron-reservoir complexes,[16] magnetic molecular materials,[17] conducting materials,[17] and biochemistry.[18,19] Moreover, being an isoelectronic species of the 1*H*-1,2,4-triazole, pyrazole, and phosphole, the 1*H*-1,2,4-diazaphosphole with the unique electronic structure is expected to be a motif in a number of small organic molecules,[1–4] or to be an excellent candidate for the investigation of intermolecular solid state proton transfer (ISSPT),[20,21] and may possess a wide range of agricultural, pharmaceutical[22] and catalytic activities.[4a,9,23] However, in contrast to 1*H*-1,2,4-triazole, pyrazole, and phosphole, the 1*H*-1,2,4-diazaphosphole chemistry is still at its early stage to date, and attempts to synthesize an extensive family of 1*H*-1,2,4-diazaphospholes have been unsuccessful since several H[3,5-R_2dp] (R = H, Ph, *t*Bu) were reported in 1984.[8,24] This has prompted us to prepare a few particularly designed 1*H*-1,2,4-diazaphospholes incorporating varied substituents at 3,5-positions with steric

and electronic effects, which are expected to be highly potential building blocks for further synthetic chemistry.[2–5,11–14,20–22] Herein, we report the synthesis of a few 1*H*-1,2,4-diazaphopholes H[3,5-R_2dp] with a variant protocol (R = methyl (**5a**), *p*-tolyl (**5b**), 1-naphthyl (**5c**), 2-furanyl (**5d**), 2-thienyl (**5e**), isopropyl (**5f**)). The X-ray diffraction analysis revealed that molecular structures of **5a-f** present intermolecular interactions with ISSPT or with N–H···N hydrogen bonding.

Chart 1.



2．Experimental

2.1. General methods

All manipulations were carried out in an argon atmosphere under anaerobic conditions using standard Schlenk, vacuum line and glove box techniques. Solvents were distilled over appropriate drying agents under argon prior to use. ^{1}H, ^{31}P{^{1}H }, and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVANCE–600 spectrometer (^{1}H NMR(600 MHz), ^{31}P{^{1}H } NMR(243 MHz), and ^{13}C{^{1}H} NMR(150 MHz)) and chemical shifts reported in ppm.

*2.2. General procedure for the preparation of compound **3***

To a solution of the corresponding *N*,*N*-dimethylamide (**2**, 187.0 mmol) in anhydrous ether (500 mL), oxalyl chloride (412.0 mmol) was slowly added under the stirring by a syringe at room temperature. After gas evolution ceased the suspension was stirred for further 6 hours and then filtered. The white solid was washed with anhydrous ether (20 mL × 3) and dried in vacuum to afford **3** as pure solid.

2.2.1. α-Chloro-N,N-dimethyl-p-tolylmethanaminium chloride (***3b***): M.p. = 80–83°C; ^{1}H NMR

($CDCl_3$, ppm) δ = 7.84, (d, 2 H, Ph), 7.33 (d, 2 H, Ph), 3.99 (s, 3 H, NCH_3), 4.01 (s, 3 H, NCH_3), 2.40 (s, 3 H, CH_3Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) δ = 173.38 (Cl*C*), 146.45, 129.99, 129.77, 129.01, 127.75 (5s, *C*Ph), 49.93 (s, N*C*), 49.06 (s, N*C*), 21.85 (s, C*C*H_3). Anal. Calcd. For $C_{10}H_{13}NCl_2$: C 55.06, H 6.01, N 6.42; Found: C 55.28, H 6.09, N 6.35.

*2.2.2. α-Chloro-N,N-dimethyl-(1-naphthyl)methanaminium chloride (**3c**)*: M.p. = 85–87°C; ^1H NMR ($CDCl_3$, ppm) δ = 8.47, 8.09, 7.94, 7.68, 7.58–7.62 (m, 7 H, 1-naphthyl ring), 4.43 (s, 3 H, NCH_3), 3.92 (s, 3 H, NCH_3); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, ppm) δ = 173.34 (s, *C*Cl), 134.10, 133.20, 129.40, 129.20, 128.20, 127.98, 125.30, 124.80, 123.50 (9s, *C* atoms on 1-naphthyl ring), 49.77 (s, N*C*), 49.21 (s, N*C*). Anal. Calcd. For $C_{13}H_{13}NCl_2$: C 61.43, H 5.16, N 5.51; Found: C 61.32, H 5.10, N 5.60.

2.2.3. α-Chloro-N,N-dimethyl-thiophylmethanaminium chloride (***3e***): M.p. = 120–121°C; ^1H NMR ($CDCl_3$, ppm) δ = 8.43 (d, 1 H, C*H*CS), 8.19 (d, 1 H, C*H*S), 7.31 (t, 1 H, C*H*CS), 4.26 (s, 3 H, NCH_3), 4.09(s, 3 H, NCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm) δ = 162.60, 162.59 (d, *C*Cl), (s, *C*Cl), 142.43, 141.97, 131.50, 130.13 (4s, *C* on 2-thienyl ring), 49.90 (s, NCH_3). Anal. Calcd. For $C_7H_9NCl_2S$: C 40.01, H 4.32, N 6.67; Found: C 40.13, H 4.22, N 6.72.

*2.3. General procedure for the preparation of compound **4***

To a solution of **3** (100.0 mmol) in anhydrous acetonitrile (250 mL), tris(trimethylsilyl)phosphine $P(SiMe_3)_3$ (3.644mmol/mL, 60.0 mmol) was slowly added by a syringe within 1 hour. The volatile components were removed under reduced pressure (0.01 mmHg). The resulting residue was washed with anhydrous ether (10 mL × 3) to give **4** as colored solid.

2.3.1. α-[[(Dimethylamino)ethylidene]phosphino]-N,N-dimethyl-methylmethanaminium chloride (***4a***): M.p. = 126–128°C; ^1H NMR ($CDCl_3$, ppm) δ = 3.53 (s, 6 H, NCH_3), 3.52 (s, 6 H, NCH_3),

2.77 (s, 6 H, CC*H*$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, ppm) δ = 81.93(s); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) δ = 171.50, 170.40 (2s, N*C*P), 43.69 (s, N*C*H$_3$), 38.02 (s, N*C*H$_3$), 21.50 (s, *C*H$_3$). Anal. Calcd. For $C_8H_{18}ClN_2P$: C 46.05, H 8.69, N 13.42; Found: C 45.95, H 8.75, N 13.01.

2.3.2. α-[[(Dimethylamino)-p-tolyl-methylene]phosphino]-N,N-dimethyl-p-tolyl-methanaminium chloride (***4b***): M.p. = 140–143°C; ^{1}H NMR ($CDCl_3$, ppm) δ = 6.25, 5.95 (m, 8 H, Ph ring), 3.26 (s, 6 H, NC*H*$_3$), 2.65 (s, 6 H, NC*H*$_3$), 1.70 (s, 6 H, *p*-tolyl–C*H*$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, ppm) δ =114.30(s); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) δ = 204.11, 203.65 (2s, N*C*P), 140.19, 134.78, 128.19, 127.58 (4s, *C* on *p*-tolyl rings), 46.22 (s, N*C*H$_3$), 46.03 (d, N*C*H$_3$), 45.57 (s, N*C*H$_3$), 20.90 (s, *p*-tolyl–*C*H$_3$). Anal. Calcd. For $C_{20}H_{26}ClN_2P$: C 66.57, H 7.26, N 7.76; Found: C 66.49, H 7.34, N 7.59.

2.3.3. α-[[(Dimethylamino)-1-naphthyl-methylene]phosphino]-N,N-dimethyl-1-naphthyl-methanaminium chloride (***4c***): M.p. = 184–187°C; ^{1}H NMR ($CDCl_3$, ppm) δ = 7.32–7.26, 7.05, 6.90, 6.49 (m, 14 H, 1-naphthyl), 3.93 (s, 6 H, NC*H*$_3$), 2.82 (s, 6 H, NC*H*$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, ppm) δ = 117.45(s); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) δ = 203.16, 202.67 (2s, N*C*P), 133.53, 133.49, 131.69, 129.61, 128.86, 128.87, 128.01, 127.61, 127.41, 126.50, 124.85, 124.57 (12s, *C* on 1-naphthyl rings), 46.34, 46.12 (d, N*C*H$_3$), 46.07 (s, N*C*H$_3$). Anal. Calcd. For $C_{26}H_{26}ClN_2P$: C 72.13, H 6.05, N 6.47; Found: C 72.35, H 6.13, N 6.38.

2.3.4. α-[[(Dimethylamino)-furanyl-methylene]phosphino]-N,N-dimethyl-furyl-methanaminium chloride (***4d***): M.p. = 155–157°C; ^{1}H NMR ($CDCl_3$, ppm) δ = 7.14, 6.39, 6.04 (m, 6 H, 2-furyl), 3.48 (s, 6 H, NC*H*$_3$), 3.13 (s, 6 H, NC*H*$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, ppm) δ = 95.28(s); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) δ = 188.11, 187.65 (2s, N*C*P), 147.59, 121.26, 112.46 (3s, *C* on 2-furanyl rings), 46.65, 46.81 (d, N*C*H$_3$), 46.23 (s, N*C*H$_3$). Anal. Calcd. For $C_{14}H_{18}ClN_2O_2P$: C 53.77, H 5.80, N 8.96; Found: C 53.89, H 5.71, N 8.84.

2.3.5. α-[[(Dimethylamino)-thienyl-methylene]phosphino]-N,N-dimethyl-thiophyl-methanaminium chloride (***4e***): M.p. = 172–174°C; ^{1}H NMR ($CDCl_3$, ppm) δ = 7.51, 6.85, 6.71 (m, 6 H, 2-thienyl), 3.80 (s, 6 H, NC*H*$_3$), 3.44 (s, 6 H, NC*H*$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, ppm) δ = 131.3(s); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) δ = 194.60, 194.15 (2s, N*C*P), 139.18, 133.61, 131.36, 128.84 (4s, *C* on 2-thienyl), 47.36 (s, N*C*H$_3$), 46.21 (s, N*C*H$_3$). Anal. Calcd. For $C_{14}H_{18}ClN_2S_2P$: C 48.76, H 5.26, N 8.12; Found: C 48.83, H 5.32, N 8.07.

2.3.6. α-[[(Dimethylamino)-iso-propyl-methylene]phosphino]-N,N-dimethyl-iso-propyl-methanaminium chloride (***4f***): M.p. = 101–103°C; ^{1}H NMR ($CDCl_3$, ppm) δ = 3.37 (br, 12 H, NC*H*$_3$), 2.49, 3.07 (m, 2 H, C*H*), 1.19 (d, 12 H, CC*H*$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, ppm) δ = 31.8(s); ^{13}C{^{1}H} NMR ($CDCl_3$, ppm) δ = 221.23 (d, $^{1}J_{P–C}$ = 6.0 Hz), 210.56 (d, $^{1}J_{P–C}$ = 6.0 Hz, N*C*P), 37.22 (s, N*C*H$_3$), 37.09 (s, N*C*H$_3$), 22.04 (s, *C*CH$_3$), 21.51 (s, *C*H$_3$). Anal. Calcd. For $C_{12}H_{26}ClN_2P$: C 54.43, H 9.90, N 10.58; Found: C 54.50, H 9.81, N 10.65.

*2.4. General procedure for the preparation of compound **5***

To a solution of **4** (10.0 mmol) in 100 mL chloroform, anhydrous hydrazine (20.0 mmol) was added slowly. The reaction mixture was stirred for 24 h at room temperature, and then heated to reflux for 48 h (only for **4a**). After the volatile components were removed under reduced pressure, water (50 mL) was added to the resulting residue. The mixture was extracted with ether (3 × 20 mL). The combined organic layers were dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The resulting solid was purified by the recrystallization from the mixed solvents of ethyl acetate and petroleum ether (1:1) or by sublimation in high vacuum (0.01 mmHg) to afford **5a** at 80°C (**5c** at 140°C, **5d** at 210°C, **5e** at 185°C, and **5f** at 45°C) as pure white solid.

2.4.1. 1H-3,5-dimethyl-1,2,4-diazaphosphole (***5a***): M.p. = 99–101°C. ^{1}H NMR (CD_3Cl, 23°C): δ = 11.21 (br., 1 H, N–*H*), 2.55 (d, 6 H , $^{3}J_{P–H}$ = 9.0 Hz, C*H*$_3$) ppm. ^{31}P{^{1}H} NMR (CD_3Cl, 23°C):

δ = 81.95 (sept. J = 9.0 Hz). $^{13}C\{^{1}H\}$ NMR (CD_3Cl, 23 °C): δ = 15.97 (very br., $\delta_{1/2}$ = 0.4 ppm, *C*H_3),[7b] 175 (br., P*C*N) ppm. Anal. Calcd. For $C_4H_7N_2P$: C 42.11, H 6.18, N 24.55; Found: C 41.95, H 6.08, N 24.46.

2.4.2. 1H-3,5-di(p-tolyl)-1,2,4-diazaphosphole (***5b***): M.p. = 257–258ºC. ^{1}H NMR (CD_3Cl, 23 °C): δ = 11.5 (br., N–H), 7.73 (d, $^{3}J_{P-H}$ = 7.2 Hz, 4 H, Ar–H), 7.27 (d, $^{3}J_{P-H}$ = 7.2 Hz, 4 H, Ar–H), 2.42 (s, 6 H, C*H*$_3$); $^{31}P\{^{1}H\}$ NMR($CDCl_3$, 23 °C): δ = 72.51 (s); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 23°C): δ = 178.20 (s, P*C*N),[7c] 139.22, 129.72, 126.09, 126.03 (4s, *C* for phenyl rings), 21.34 (s, *C*H_3). Anal. Calcd. For $C_{16}H_{15}N_2P$: C 72.17, H 5.68, N 10.52; Found: C 71.98, H 5.60, N 10.42.

2.4.3. 1H-3,5-di(1-naphthyl)-1,2,4-diazaphosphole (***5c***): M.p. = 167–169°C. ^{1}H NMR (CD_3Cl, 23°C): δ = 9.5 (very br., 1 H, N–*H*), 8.44 (d, $^{3}J_{P-H}$ = 7.8 Hz, 2 H), 7.92–7.94 (m, overlapped, 4 H), 7.76 (d, $^{3}J_{P-H}$ = 7.0 Hz, 2 H), 7.54–7.57 (m, overlapped, 6 H). $^{31}P\{^{1}H\}$ NMR (CD_3Cl, 23°C): δ = 94.33 (s) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3Cl, 23 °C): δ = 175.99 (d, $^{1}J_{P-C}$ = 73.5 Hz, P*C*N), 131.37 (d, $^{2}J_{P-C}$ = 16.5 Hz, ipso–*C*), 127.82 (d, $^{3}J_{P-C}$ = 24 Hz, PC*C*), 125.55 (d, $^{3}J_{P-C}$ = 17.4 Hz, PC*C*), 131.15 (d, $^{4}J_{P-C}$ = 6.0 Hz, PCC*C*), 125.32, 126.26, 126.91, 128.48, 129.49, 133.97 (6s, *C* for naphthyl rings) ppm. Anal. Calcd. For $C_{22}H_{15}N_2P$: C 78.10, H 4.47, N 8.28; Found: C 78.40, H 4.48, N 8.24.

2.4.4. 1H-3,5-difuranyl-1,2,4-diazaphosphole (***5d***): M.p. = 235–237°C. ^{1}H NMR (CD_3Cl, 23°C): δ = 11.91 (br., 1 H, N–*H*), 7.43 (d, $^{4}J_{P-H}$ = 18 Hz, 2 H), 6.79 (d, $^{3}J_{P-H}$ = 36.0 Hz, 2 H), 6.453, 6.447 (dd, $^{4}J_{P-H}$ = 18.0 Hz, 2 H) ppm. $^{31}P\{^{1}H\}$ NMR (CD_3Cl, 23°C): δ = 69.85 (s) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3Cl, 23 °C): δ = 142.62 (d, $^{3}J_{P-C}$ = 12.0 Hz, PCC*C*), 148.52 (br., *ipso–C*), 166.0 (br., P*C*N), 142.61, 111.95, 108.17 (3s, *C* for furanyl rings) ppm. Anal. Calcd. For $C_{10}H_7N_2O_2P$: C 55.06, H 3.23, N 12.84; Found: C 54.86, H 3.20, N 12.75.

2.4.5. 1H-3,5-dithienyl-1,2,4-diazaphosphole (***5e***): M.p. = 206–207°C. ^{1}H NMR (CD_3Cl, 23°C):

δ = 11.0 (br., 1 H, N–*H*), 7.43 (d, $^{3}J_{P–H}$ = 36 Hz, 2 H), 7.33 (d, $^{4}J_{P–H}$ = 48 Hz, 2 H), 7.07 (dd, overlapped, 2 H) ppm. $^{31}P\{^{1}H\}$ NMR (CD_3Cl, 23°C): δ = 74.96 (s) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3Cl, 23°C): δ = 170.5 (d, $^{1}J_{P–C}$ = 51.0 Hz, P*C*N), 126.33 (d, $^{2}J_{P–C}$ = 12.0 Hz, PC*C*), 125.76 (d, $^{3}J_{P–C}$ = 4.5 Hz, PCC*C*), 127.99 (s, *C* for thienyl rings), 126.35 (br., *C*S) ppm. Anal. Calcd. For $C_{10}H_7N_2PS_2$: C 47.99, H 2.82, N 11.19; Found: C 47.76, H 2.83, N 11.14.

2.4.6. 1H-3,5-diisopropyl-1,2,4-diazaphosphole (***5f***): M.p. = 62–65 °C. ^{1}H NMR (CD_3Cl, 23°C): δ = 11.4 (br., 1 H, N–*H*), 1.38 (d, 6 H , $^{3}J_{P–H}$ = 6.6 Hz, CH_3), 3.22 (sept. 2 H, C*H*), $^{31}P\{^{1}H\}$ NMR (CD_3Cl, 23°C): δ = 66.85 (s). $^{13}C\{^{1}H\}$ NMR (CD_3Cl, 23 °C): δ = 24.43, 24.39 (d, $^{3}J_{P–C}$ = 6.0 Hz, *C*H_3), 30.85, 30.75 (d, $^{2}J_{P–C}$ = 15.0 Hz, *C*H), 186.8, 186.5 (d, $^{1}J_{P–C}$ = 45.0 Hz, P*C*N) ppm. Anal. Calcd. For $C_8H_{15}N_2P$: C 56.46, H 8.88 N 16.46; Found: C 56.53, H 8.30, N 16.61.

2.5 Computational details

To understand the nature of proton disorder and the intermolecular hydrogen bonds about **5b–c**, we have performed a series calculations on two static hydrogen-bonding models **5bm** (**5cm**) using Gaussian 03 program package.[25] We first compared the results with B3LYP and MP2 methods on a simplified 1*H*-1,2,4-diazaphosphole dimer for the geometrical optimization, respectively. Both of the methods give, however, almost identical values, indicating that B3LYP method is reliable to obtain the geometries of **5bm** and **5cm**.[26] Therefore, the monomer and dimer of **5bm** and **5cm** are optimized at the B3LYP/6-311++G** level.[26] All harmonic frequencies are real for the stable structures.

2.6 X-ray crystallography

The single-crystal X-ray diffraction data of **5** were collected using a Bruker SMART CCD diffractometer operating at 50 kV and 20 mA using Mo-Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program. The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement

by full-matrix least squares on F^2 using the SHELXTL package.[27] The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All non-hydrogen atoms were found from the difference Fourier syntheses. All calculations were performed using the Bruker Smart program.

CCDC 938848(**5a**), 938849(**5b**), 938850(**5c**), 938851(**5d**), 938852(**5e**), and 938853(**5f**) contain the supplementary crystallographic data for compound **5**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or email: data_request@ccdc.cam.ac.uk.

3. Results and discussion

3.1 Synthesis

As shown in Scheme 1, *N*,*N*-dimethylimidoyl chloride **3** was prepared by the acylation of RCOCl (**1**) with Me_2NH, followed treatment with oxalyl chloride, or simply by the reaction of the commerical available *N*,*N*-dimethylamide $RCONMe_2$ (**2**)[28,29] and oxalyl chloride in anhydrous ether. Compound **3** presents colors in green (**3a**), white (**3b**, **3f**), yellow-white (**3c**), and milky (**3d**, **3e**), respectively. The treatment of **3a–f** with $P(SiMe_3)_3$[30] in anhydrous acetonitrile afforded the corresponding 1,3-bis(dimethylamino)-2-phosphoallyl chlorides **4a** (black), **4b–f** (yellow to reddish-brown) in good yields. The chemical shifts of **4a–f** in $^{31}P\{^1H\}$ NMR spectra extend over a remarkably large range (Table 1).

Scheme 1. Synthesis of compounds **3–5**, and the possible dynamic situation of **5** in solid state.

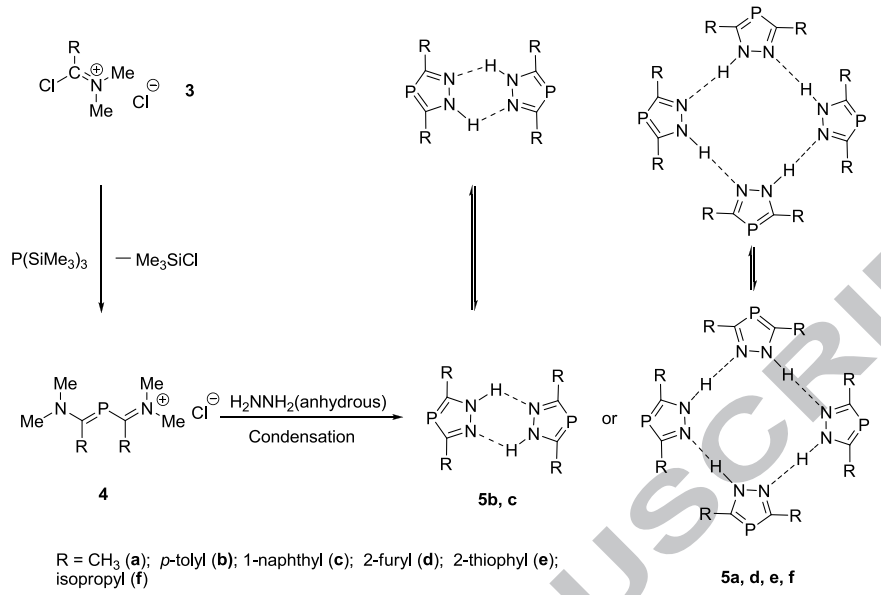


Table 1. Preparation of compounds **3**, **4**, and **5** with varied substituted groups

Entry	**reactant**	reagent	R	**product**	^{31}P NMR, δ (ppm)	Yield (%)
1	**2b**	Me_2NH	*p*-tolyl	**3b**	–	75
2	**2c**	Me_2NH	1-naphthyl	**3c**	–	79
3	**2e**	Me_2NH	2-thienyl	**3e**	–	89
4	**3a**	$P(SiMe_3)_3$	methyl	**4a**	89.6(s)	93
5	**3b**	$P(SiMe_3)_3$	*p*-tolyl	**4b**	105.6(s)	88
6	**3c**	$P(SiMe_3)_3$	1-naphthyl	**4c**	117.9(s)	78
7	**3d**	$P(SiMe_3)_3$	2-furanyl	**4d**	95.3(s)	73
8	**3e**	$P(SiMe_3)_3$	2-thienyl	**4e**	131.0(s)	78
9	**3f**	$P(SiMe_3)_3$	isopropyl	**4f**	31.8(s)	83
10	**4a**	H_2NNH_2	methyl	**5a**	81.95(sept.), ^3J = 9.0Hz	16
11	**4b**	H_2NNH_2	*p*-tolyl	**5b**	72.5(s)	79
12	**4c**	H_2NNH_2	1-naphthyl	**5c**	94.3(s)	85
13	**4d**	H_2NNH_2	2-furanyl	**5d**	69.9(s)	80
14	**4e**	H_2NNH_2	2-thienyl	**5e**	75.0(s)	82
15	**4f**	H_2NNH_2	isopropyl	**5f**	66.9(s)	61

The titled compounds **5a–f** were prepared by the reaction of dry hydrazine at ambient temperature with **4b–f** and at reflux with **4a** (Scheme 1), respectively. The small amount of moisture in the system, such as using hydrazine hydrate, will lead to the significant yield decrease of **5**, likely due to hydrolysis of reactant **4**. Compound **5** can be isolated by the

sublimation (except for **5b**) in high vacuum using a Büchi Glass Oven (B–585) or by the recrystallization from the mixed solvents of ethyl acetate and petroleum ether (1:1), exhibiting sharp, reversible melting points at 99°C (**5a**), 257°C (**5b**), 167°C (**5c**), 235°C (**5d**), 206°C (**5e**), and 63°C (**5f**). The compound **5** is very soluble in CH_3Cl and CH_2Cl_2 and well soluble in THF and ether, but not soluble in *n*-hexane. All compounds were obtained in fair or good yields except for **5a** (Table 1). We tried to improve the low yield of **5a** by optimizing the reaction condition or by using varied amines such as diphenylamine or di-*c*-hexylamine as a starting material, but not successful.

3.2 NMR Spectra

^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectra and element analysis data are consistent with the formulas of **3b–e**, **4**, and **5**.[26] Compounds (**4a-f**) are asymmetric cations, therefore, in $^{13}C\{^{1}H\}$ NMR spectra, two doublets are expected for two equivalent carbon atoms ($^{1}J_{P\text{-}C}$) with different $^{1}J_{P\text{-}C}$ values. As expected, two doublets were observed for **4f** in $^{13}C\{^{1}H\}$ NMR spectrum but only two singlets were found for **4a-4e**, probably due to the consequence of a dynamic process in solution. In the ^{1}H NMR spectra, compound **5** exhibits broad resonances at δ = 9.5–11.9 ppm ($CDCl_3$) for NH absorptions (one doublet at δ = 2.56 ppm ($CDCl_3$) assigned to CH_3 groups for **5a**), indicating the dynamic process of N–H···N hydrogen bonds (P–CH_3 coupling) in the solution. In the $^{13}C\{^{1}H\}$ NMR spectrum of **5a**, an unusual broad signal at δ = 15.97 ppm ($\delta_{1/2}$ = 0.4 ppm) was observed, attributable to the *C*H_3 groups in the solution on account of the dynamic process of tautomeric **5a** (probably due to overlapped P–C coupling signals) being relatively slow on the $^{13}C\{^{1}H\}$ NMR time scale. The $^{31}P\{^{1}H\}$ NMR septet resonance at δ = 81.95 ppm ($^{3}J_{P–H}$ = 9.0 Hz) for **5a** seems due to the results of the spin coupling with the six methyl protons (*versus* the triplet resonance at δ = 82.8 ppm ($^{1}J_{P–H}$ = 44.1 Hz) for P–C*H* in H[dp])[8] while the exclusively observed sharp $^{31}P\{^{1}H\}$ NMR single resonances suggest the formation of **5b**–**5f** (Table 1). However, attempt to elucidate the dynamic situation of N–H···N hydrogen bonding was not successful in the solutions at varied temperatures and only the broader resonances were

observed for NH absorptions. At this point, we have noted that the dynamic process for N–H···N hydrogen bonds of ^{15}N labeled pyrazoles was elucidated by ^{15}N NMR spectroscopy under varied temperatures.[21] Notably, the expected doublets resulting from P–C coupling ($^{1}J_{P-C}$) were not observed for **5a** and **5b**, probably due to the broad resonances.[7b,26]

3.3 Structure conformatios in solid state

The crystal structures of **5a**, and **5d–f** featured cyclic tetramers that present a pseudo 42m (D_{2h}) internal symmetry, of which only a 2-fold axis remains as a crystallographic element while **5b–c** formed cyclic dimers with a pseudo 2-fold axis (Table 2).[26,27] All structures present exclusively the NH···N hydrogen bond bridges in solid state, by which the molecules are linked into oligomers. The intermolecular hydrogen bonds of **5** in the solid state are evidenced by the special molecular orientation in the packing diagram.[26] No any P**–**H tautomeric structure was observed, consistent with the recently theoretical calculation results.[31] The small difference between two nitrogen internal angles for **5** (except for **5f**) is likely attributable to the disordered NH protons (Table 3).

Table 2. Crystal and Data Collection Parameters of Compounds **5a-f**

Compounds	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**
formula	$C_4H_7N_2P$	$C_{32}H_{30}N_4P_2$	$C_{22}H_{15}N_2P$	$C_{10}H_7N_2O_2P$	$C_{10}H_7N_2PS_2$	$C_8H_{15}N_2P$
fw	114.09	532.54	338.33	218.15	250.27	170.19
Cryst. size (mm)	0.10 × 0.03 × 0.03	0.27 × 0.25 × 0.18	0.49 × 0.36 × 0.10	0.08 × 0.03 × 0.02	0.45 × 0.28 × 0.11	0.30 × 0.20 × 0.20
Cryst. Syst.	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*-1	*P*2(1)/*c*	*C*2/*c*	*C*2/*c*	P2(1)/c
a (Å)	8.6220(5)	9.6653(16)	8.670(2)	12.7274(2)	26.914(5)	19.7027(18)
b (Å)	9.8843(6)	9.6809(16)	8.036(2)	19.2423(3)	9.9285(19)	10.7761(10)
c (Å)	15.4697(10)	16.449(3)	24.936(7)	16.9663(3)	20.764(4)	27.0431(18)
α(deg)	80.166(4)	74.227(3)	90	90	90	90
β(deg)	89.008(4)	75.002(3)	97.589(3)	93.2190(10)	126.155(2)	132.144(4)
γ(deg)	75.641(4)	75.181(3)	90	90	90	90
V (Å^3)	1257.98(13)	1402.0(4)	1722.2(8)	4148.57(12)	4480.0(15)	4257.3(6)
Z	8	2	4	16	16	16
Dc (g cm^{-3})	1.205	1.257	1.305	1.397	1.484	1.062
Absorption coefficient (mm^{-1})	0.318	0.183	0.165	0.244	0.583	0.207

F (000)	480	560	704	1792	2048	1472
T (K)	296	298	298	296	298	238
range (deg)	1.34 – 25.00	1.31 – 27.00	2.37 – 25.50	2.12 – 25.00	1.87 – 25.50	1.39 - 24.15
reflns measured	17353	7460	8612	13345	11531	18218
unique reflns	4423	5883	3197	3546	4149	6806
θ_{max} (deg)	25.00	27.00	25.50	25.00	25.50	25.00
R_{int}	0.0435	0.0257	0.0230	0.0283	0.0360	0.0691
Max and min Transmn	0.9905 and 0.9689	0.9678 and 0.9522	0.9837 and 0.9234	0.9951 and 0.9807	0.9386 and 0.7794	0.9598 and 0.9405
*R*1, *wR*2 [$I > 2\sigma(I)$][a]	0.0979, 0.2695	0.0859, 0.2478	0.0453, 0.1110	0.0652, 0.1820	0.0658, 0.1594	0.0618, 0.1243
*R*1, *wR*2 (all data)[b]	0.1272, 0.2875	0.1239, 0.2892	0.0550, 0.1174	0.0957, 0.2122	0.1022, 0.1836	0.1848, 0.1729
GOF	1.070	1.098	1.031	1.036	1.025	0.954
Δ□(max) (e□Å^{-3})	0.965	0.706	0.342	0.254	0.422	0.203
Δ□(min) (e□Å^{-3})	–0.345	–0.431	–0.185	-0.262	-0.343	-0.195

[a] $R1 = \Sigma|Fo| - |Fc|/\Sigma|Fo|$. [b] $wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{0.5}$.

As far as the molecular structure of **5a** is concerned (Fig. 1), the influence of phosphorus atom is manifested in the tetrameric conformation of **5a** compared to that of cyclic trimeric 3,5-dimethyl-pyrazole.[21] At this point, the distorted tetrameric geometry of **5a** may be less favorable to the concerted proton migration as trimeric 3,5-dimethyl-pyrazole.[21] The bond lengths and angles of **5a** (Table 3) are slightly longer and less acute than those found in H[dp] (P(1)–C(3) 1.710(3) Å, N(1)–C(2) 1.305(3) Å, N(1)–N(2) 1.323(3) Å, C(3)–P(1)–C(2), 85.1(1)°).[20a]

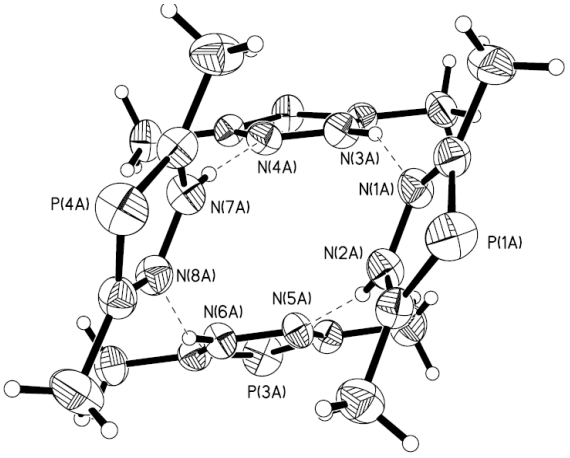


Figure 1. Crystal structure of **5a**. Bond distances [Å] and angles [deg.] are located in Table 3.

As illustrated in Figures 2–3, the average planes formed by *p*-tolyl (naphthyl) groups and the heterocycle ring are not coplanar (twisted) in **5b** (**5c)**. The dihedral angles are likely caused by an intramolecular interaction of adjacent groups due to a repulsive interaction between the CH of *p*-tolyl (or naphthyl) groups and the NH.[20b] The conformation of **5b** is similar to that found in previously reported 1*H*-3,5-diphenyl-1,2,4-diazaphosphole.[20b] However, it is surprising that **5c** presents only one molecular conformation with much more twisted one (the average naphthyl dihedral is 46.1(1)°), obviously rising from the steric effects of the bulky naphthyl groups. The remarkable feature of the structures **5b-c** is that the difference of the internal angles between at N(1) and N(2) are much larger, for example in **5b** (115.5(4)° vs. 111.1(4)°), than that found in **5a** (115.1(5)° vs. 112.2(6)°), probably suggesting that the tautomers are less stable (Table 3). The bond lengths and angles of **5b** and **5c** (Table 3) are comparable with those found in H[3,5-Ph_2dp] (P(1)–C(1) 1.7404(18) Å, N(1)–C(1) 1.329(2) Å, N(1)–N(2) 1.341(2) Å, C(3)–P(1)–C(2), 87.16(9)°).[20b]

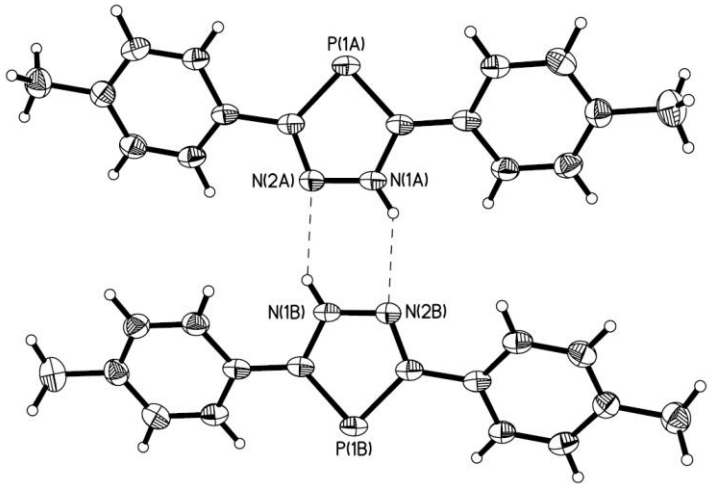


Figure 2. Crystals structure of **5b**. Bond distances [Å] and angles [deg.] are located in Table 3.

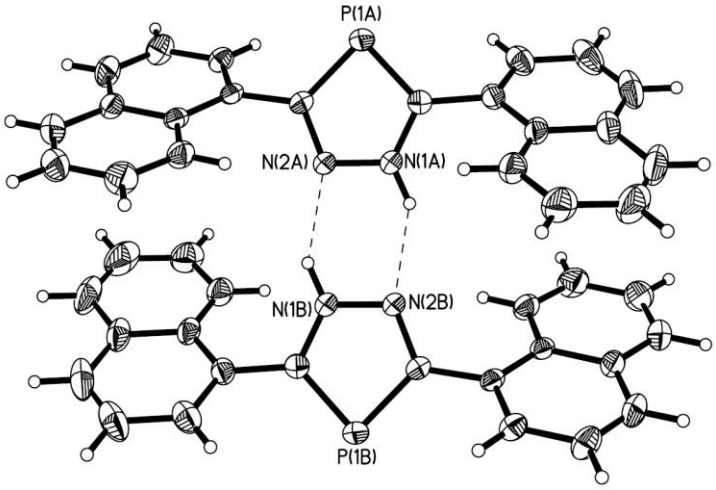


Figure 3. Crystal structure of **5c**. Bond distances [Å] and angles [deg.] are located in Table 3.

Table 3. Selected Bond Distances [Å] and Angles [deg.] for **5**

Compound	N1–N2	N1–C2	P1–C2	C3–P1–C2	C2–N1–N2	C3–N2–N1
5a	1.352(7)	1.319(8)	1.748(8)	87.2(3)	112.2(6)	115.1(5)
5b	1.358(5)	1.351(5)	1.751(5)	87.2(2)	111.1(4)	115.5(4)
5c	1.346(2)	1.327(2)	1.741(2)	87.21(8)	111.7(6)	115.5(2)
5d	1.333(4)	1.331(4)	1.730(4)	86.11(18)	111.6(3)	114.6(3)
5e	1.349(4)	1.323(4)	1.742(4)	86.63(17)	113.4(3)	113.3(3)
5f	1.347(5)	1.337(5)	1.721(5)	87.0(3)	109.9(5)	116.0(5)

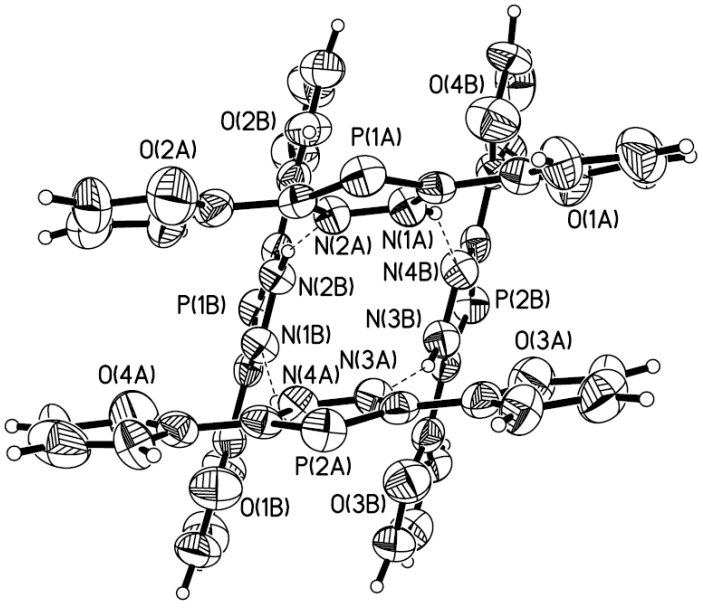


Figure 4. Crystal structure of **5d**. Bond distances [Å] and angles [deg.] are located in Table 3.

The crystal structures of **5d** and **5e** can be seen in Figures 4 and 5, respectively. The crystallographic symmetry imposed a 2-fold axis through the molecules. The tetramers are held together by four symmetry related hydrogen bonds. Due to the different orientation of two furanyl (thienyl) groups to the heterocycle, there are two independent molecular conformations for **5d** ($\mathbf{A}_{5d}$ and $\mathbf{B}_{5d}$) and **5e** ($\mathbf{A}_{5e}$) and ($\mathbf{B}_{5e}$), respectively. Two oxygen (sulfur) atoms at furanyl (thienyl) rings are at the orientation to the nigrogen atoms of the heterocycle (**A**) while one of two oxygen (sulfur) atoms is at opposite position of nitrogen atoms (**B**). The tetrameric structural conformation of **5d** (**5e**) thus consists from two independent **A** and **B**, respectively. In sharply contrast to the conformation of **5b**, the furanyl and thienyl rings attached to the heterocycle are almost coplanar (only slightly twisted) and the average dihedral angle of furanyl (thienyl) groups and heterocycle ring is only 3.3(2)° (**5d**) (8.115(171)° for **5e**), respectively, probably due to the absence of a repulsive interaction between the O(S) and the NH.[20b] The bond lengths and angles of **5d** and **5e** (Table 3) are comparable with those found in H[3,5-*t*Bu$_2$dp] (P(1)–C(1) 1.737(5) Å, N(1)–C(1) 1.330(5) Å, N(1)–N(2) 1.360(5) Å, C(3)–P(1)–C(2), 87.3(2)°).[20a]

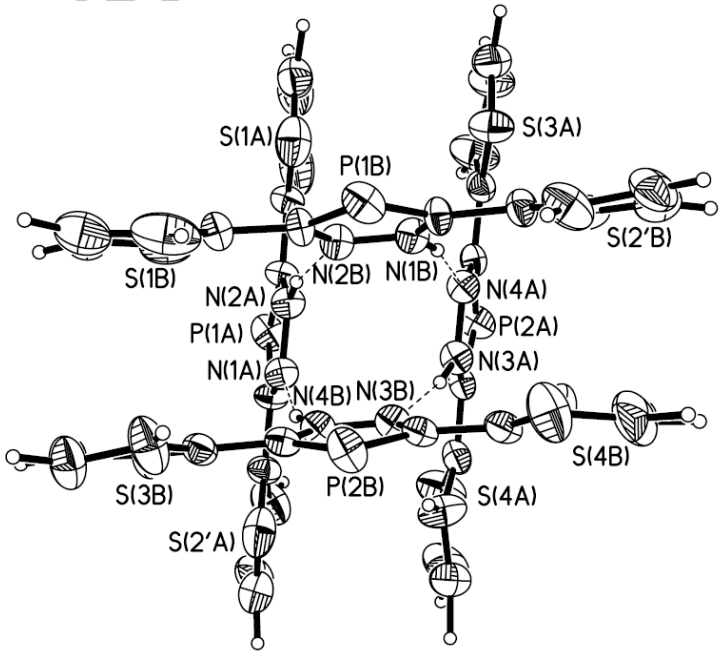


Figure 5. Crystal structure of **5e**. Bond distances [Å] and angles [deg.] are located in Table 3.

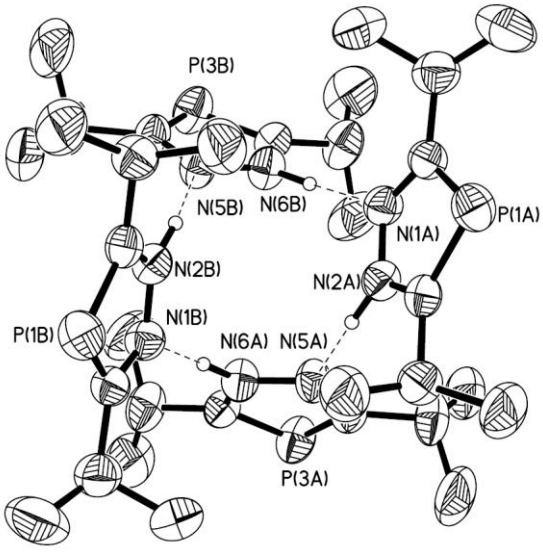


Figure 6. Crystal structure of **5f**. Bond distances [Å] and angles [deg.] are located in Table 3.

As shown in Figure 6, the molecular structure of **5f** presents in a tetrameric conformation, quite similar to that found in **5a**. Unfortunately, we cannot compare the structure of **5f** with that of corresponding 1*H*-3,5-diisopropylpyrazole because the structure of the latter is still unknown owing to its syrupy appearance.[33] Only the structure of 1*H*-3,5-diisopropyl-4-nitropyrazole, solved by X-ray powder diffraction analysis, was reported in a dimeric conformation.[33] The influence of the phosphorus atom is thus demonstrated again in the difference in the conformation compared to that of dimeric 1*H*-3,5-diisopropyl-4-nitropyrazole.[33] Notably, the difference of the internal nitrogen angles is up to 7° (Table 3), significantly larger than those found in **5a-e**. This may suggest that compound **5f** present much less intermolecular solid state proton transfer (ISSPT) and the N–H proton is thus much localized, probably owing to the bulky isopropyl groups.

Although the **5b–c** structures are somewhat similar to those of H[3,5-Ph_2dp] (two dimers),[20b] H[3,5-*t*Bu_2dp] (dimer),[20a] and 3,5-di-*tert*-butylpyrazole (dimer),[32] the present tetrameric feature of **5a**, and **5d–f** are in sharply contrast to the trimeric helix H[dp][20a] and trimeric

3,5-dimethylpyrazole,[21a] represents a new motif of hydrogen-bonded 1*H*-1,2,4-diazaphospholes to date.

3.4 Analysis of hydrogen bonding

On the basis of the difference between two nitrogen internal angles, the positions of NH protons seemed neither localized nor freely refined. Nevertheless, the data are sufficient for a general structural characterization and have presented some useful information for the preliminary discussion of hydrogen bridging phenomena and proton disorder (Table 4).

Table 4. Geometrical parameters of **5bm** and **5cm** obtained at the B3LYP/6-311++G** level and the corresponding experimental values of **5b** and **5c** (bond lengths (Å) and angles (°))

		5bm (R = *p*-tolyl)		**5b**	**5cm** (R = 1-naphthyl)		**5c**
		$monomer_{calcd}$	$dimer_{calcd}$	$dimer_{exp}$	$monomer_{calcd}$	$dimer_{calcd}$	$dimer_{exp}$
C–N(2)–N(1)	6-311++G**	118.9	118.1	115.5(4)	119.1	118.3	115.5(2)
C–N(1)–N(2)	6-311++G**	109.4	110.0	111.1(4)	109.4	110.1	111.7(6)
N(1A)···N(2B)	6-311++G**	–	2.940	2.898	–	2.925	2.823

Considering the proton is static, the optimized dimeric **5bm**(**5cm**) structure is close to that of monomeric **5bm**(**5cm**), represented by a small difference (no more than 1°) at the corresponding internal nitrogen angles, suggesting the hydrogen bonds are with the negligible effect on the conformation. Showing a difference 9.5°, two internal nitrogen angles in monomeric **5bm** are 118.9° and 109.4°, close to the ideal values of sp^2- and sp^3-hybridized nitrogen atoms, respectively. Similarily, this difference is 8.1°(118.1°–110.0°) in dimeric **5bm**, only deviating 1.4° from that of monomeric **5bm**.

The experimental results shown, however, that the difference of two internal nitrogen angles is only 4.4° for **5b**, much smaller than the calculation value (9.5° and 8.1°) for monomeric and dimeric **5bm**. The significant differences between computational results of hydrogen-bonding model **5bm** and the experimental values are presumably ascribed to a certain degree of ISSPT in crystal **5b**, which results in an equalization of two internal nitrogen angles. In addition,

calculation results presented that the linear distance N(1A)···N(1B) between two diazaphosphole rings is 2.940 Å, longer than the experimental value (2.898 Å). This change might be regarded as the additional consequence of ISSPT. The calculation results for **5cm** afforded the similar conclusion to those of **5bm**, presumably indicating that **5c** are in an amount of dynamic proton disorder with ISSPT as well.

Upon the experimental and calculating results, it can be concluded that a small difference of two internal nitrogen angles origins to some extent from the hydrogen transfer (**5a**–**5e**) while a large difference of two internal nitrogen angles indicates the hydrogen bonding in solid state (**5f**).

The hydrogen bonding lengths, angles and the position of hydrogen atoms varied significantly.[26] For example, the nitrogen-hydrogen bond length d(D-H), hydrogen bond length d(H···A) and the hydrogen bond angle <(DHA) are 0.86 Å, 2.10 Å, and 150.1° for **5a** whereas these values are 1.00 Å, 1.93 Å, and 162° for **5f**, respectively. The differences are probably due to the effect of the substutuents at 3,5-position. It is notable that the bond lengths of N=N (1.333(4)–1.352(7) Å), N–C (1.319(8)–1.351(5) Å), P–C (1.721(5)–1.751(5) Å) and the C–P–C angle (86.11(18)–87.21(8)°) in **5** are comparable with those found in previously known 1*H*-1,2,4-diazaphospholes,[20] indicating the stability of the heterocycle.

We also calculated the NICS-values of the heterocyclic ring of **5bm**. The difference between the NICS(0)-values of monomeric and dimeric **5bm** (-13.8 for monomeric **5bm** and -12.2 for dimeric **5bm**) are rather small, so the hydrogen bonds have little effect on the aromaticity of the heterocyclic system

4. Conclusion

In summary, we have prepared and structurally characterized a few of 1*H*-1,2,4-diazaphospholes, some of which present in a new motif with hydrogen bonds in solid state. Both the experimental and theoretical results suggested that **5a–e** might be good candidates for intermolecular solid state proton transfer (ISSPT). The successful preparation and isolation of **5** are a new addition to 1*H*-1,2,4-diazaphosphole chemistry, which are highly potential as

versatile building blocks in organic radical chemistry,[13,14] organometallic syntheses,[2,12,13] chemical materials,[3–5,11] drug design[22] as well as intermolecular solid state proton transfer study.[20–21,31]

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Appendix A. Supplementary data

The X-ray crystallographic and spectroscopic data, the crystallographic plots of **5**, and the details of the density functional calculation for **5bm** and **5cm** are contained in the Supporting Information. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/xxx/xxx.

References

[1] K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy: From Organophosphorus to Phospha-organic Chemistry, Wiley & Sons, West Sussex, 1998.

[2] L. Weber, Angew. Chem. Int. Ed. 41 (2002) 563.

[3] M.P. Washington, V.B. Gudimetal, F.L. Laughlin, N. Deligonul, S. He, J.L. Payton, M.C. Simpson, J.D. Protasiewicz, J. Am. Chem. Soc. 132 (2010) 4566.

[4] (a) F. Mathey, Angew. Chem. Int. Ed. 42 (2003) 1578; (b) S. Graule, M. Rudolph, W. Shen, J.A.G. Williams, C. Lescop, J. Autschbach, J. Crassous, R. Réau, Chem. Eur. J. 16 (2010) 5976.

[5] (a) C. Romero-Nieto, S. Durben, I.M. Kormos, T. Baumgartner, Adv. Funct. Mater. 19 (2009) 3625; (b) Y. Matano, A. Saito, T. Fukushima, Y. Tokudome, F. Suzuki, D. Sakamaki, H. Kaji, A. Ito, K. Tanaka, H. Imahori, Angew. Chem. Int. Ed. 50 (2011) 8016.

[6] L. Nyulászi, T. Veszprémi, J. Réffy, B. Burkhardt, M. Regitz, J. Am. Chem. Soc. 114 (1992) 9080.

[7] (a) S.P. Visser: The replacement of a nitrogen atom or CH group by a phosphorus atom may lead a significant electron effect on molecules, J. Phys. Chem. B. 110 (2006) 20759; (b) The ovservation of the broad P–C coupling ransonance ($^2J_{P–C}$) for **5a** is likely the consequence of recording the spectrum around the coalescence temperature; (c) The expected doublet ($^1J_{P–C} \approx 53$ Hz) was not observed for **5b**, only a singlet was observed at $\delta = 178.2$ ppm: J. Elguero, I. Alkorta, Spectroscopy 15 (2001) 27.

[8] A. Schmidpeter, A. Willhalm, Angew. Chem. Int. Ed. Engl. 23 (1984) 903.

[9] F. Mathey, Chem. Rev. 88 (1988) 429.

[10] J. Elguero, In Comprehensive Heterocyclic Chemistry; A.R. Katritzky, C.W. Rees, K.T. Potts, Eds. Pergamon Press: Oxford, U.K. 5 (1984) 167.

[11] Y. Ji, Y. Qian, W.J. Lu, Mater. Chem. 22 (2012) 12375.

[12] (a) W. Zheng, G.Z. Zhang, K.N. Fan, Organometallics 25 (2006) 1548; (b) L. Wan, C.F. Pi, L. Zhang, W. Zheng, L.H. Weng, Z.X. Chen, Y. Zhang, Chem. Commun. 2008, 2266; (c) J. Yorke, L. Wan, A.B. Xia, W. Zheng, Tetrahedron Lett. 48 (2007) 8843; (d) W. Zheng, I. Alkorta, D.M. Yang, L. Wan, M. Zhao, J. Elguero, Inorg. Chem. 50 (2011) 12408; (e) P. Schramm, A. Leineweber, F. Lissner, D. Gudat, Chem. Eur. J. 16 (2010) 2982.

[13] C.F. Pi, Y. Wang, W. Zheng, L. Wan, H.Y. Wu, L.H. Weng, L.M. Wu, Q.S. Li, P.V. R. Schleyer, Angew. Chem. Int. Ed. 49 (2010) 1842.

[14] (a) L.D. Quin, Curr. Org. Chem. 10 (2006) 43; (b) L. Cataldo, S. Choua, T. Berclaz, M. Geoffroy, N. Mézailles, L. Ricard, F. Mathey, P. Le Floch, J. Am. Chem. Soc. 123 (2001) 6654.

[15] B.M. Rosen, V. Percec, Chem. Rev. 109 **(**2009) 5069.

[16] D. Astruc, New J. Chem. 33 (2009) 1191.

[17] M. Fourmigue, Acc. Chem. Res. 37 (2004) 179.

[18] S.W. Ragsdale, Chem. Rev. 106 (2006) 3317.

[19] V. Brezová, D. Dvoranová, V. Žúbor, M. Breza, M. Mazúr, Molecular Biotechnology. 37 (2007) 48.

[20] (a) K. Polborn, A. Schmidpeter, G. Märkl, A.Z. Willhalm, Naturforsch. B, 54b (1999) 187; (b) L. Wan, I. Alkorta, J. Elguero, J. Sun, W. Zheng, Tetrahedron. 63 (2007) 9129.

[21] (a) A. Baldy, J. Elugero, R. Faure, M. Pierrot, E.J. Vincent, J. Am. Chem. Soc. 107 (1985) 5290; (b) J.A.S. Smith, B. Wehrle, F. Aguilar-Parrilla, H.H. Limbach, C. Foces-Foces, F.H. Cano, J. Elugero, A. Baldy, M. Pierrot, M.M.T. Khurshid, J.B. Larcombe-MeDouall, J. Am. Chem.Soc. 111 (1989) 7304; (c) F. Aguilar-Parrilla, G. Scherer, H.H. Limbach, C. Foces-Foces, F.H. Cano, A.S. Smith, C. Toiron, J. Elguero, J. Am. Chem. Soc. 114 (1992) 9657.

[22] T.A. Riley, S.B. Larson, T.L. Avery, R.A. Finch, R.K. Robins, J. Med. Chem. 33 (1990) 572.

[23] S. Fustero, M. Sánchez-Roselló, P. Barrio, A. Simón-Fuentes, Chem. Rev. 111 (2011) 6984.

[24] A few of asymmetrical 1*H*-3,5-disubstituted-diazaphospholes were prepared by [2+3] cycloaddition of hydrocarbon-substituted phosphoaalkynes (phosphaalkenes) such as *t*BuC≡P (ClP=C(SiMe$_3$)Ph) with diazomethane RCH=N$_2$, but these routes are exclusively involved in the cumbersome preparation of low-yield starting material

phosphaalkynes and phophaalkenes, see: (a) W. Rösch, M. Regitz, Angew. Chem. Int. Ed. Engl. 23 (1984) 900; (b) G. Märkl, I. Troetsch, Angew. Chem. Int. Ed. Engl. 23 (1984) 901; (c) S. Ito, H. Miyake, M. Yoshifuji, Eur. J. Inorg. Chem. (2007) 3491; (d) P. Dianous, S. Himdi-Kabbab, J. Hamelin, Heteroatom Chem. 6 (1995) 403; (e) J. Grobe, D. Le Van, M. Hegemann, B. Krebs, M. Läge, Chem. Ber. 125 (1992) 411; (f) W. Schnurr, M. Regitz, Synthesis (1989) 511.

[25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A., Jr. Montgomery, T.Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Ehara, M. Hada, K.Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A.Voth, P. Salvador, J.J. Dannenberg, V.G. Dapprich, S. Zakrzewski, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc.; Wallingford, CT, 2004.

[26] See the Supporting Information.

[27] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Refinement, Göttingen University, Germany 1997.

[28] While **2a** and **2f** are commercial available, compounds **2b–e** were prepared referred to the literature: A.J. Speziale, R.C. Freeman, Org. Synth. 5 (1973) 387.

[29] (a) C. Belzecki, E. Rogalska, J. Chem. Soc., Chem. Commun. 1981 57; (b) M.Grdinic, V. J. Hahn, J. Org. Chem. 30 (1965) 2381; (c) B. Haveaux, A. Dekoker, M. Rens, A.R. Sidani, J. Toye, L. Ghosez, Org. Synth. 59 (1980) 26.

[30] G. Becker, H. Schmidt, G. Uhl, W. Uhl. Inorg. Synth. 27 (1990) 243.

[31] W.P. Oziminski, Comput. Theoret. Chem. 980 **(**2012) 92.

[32] A.N. Sobolev, A.H. White, Acta Cryst. 60 (2004) 621.

[33] L.E. Ochando, J.M. Amigó, J. Rius, D. Louër, C. Fontenas, J. Elguero, J. Mol. Struct. 562 (2001) 11.

Highlight

►Six previously inaccessible 1*H*-1,2,4-diazaphospholes were prepared and structurally characterized.

►All compounds are exclusively via the bridges of NH···N hydrogen bonds in solid state, by which the molecules are linked into oligomers.

► The tetrameric feature of the compounds represents a new motif of hydrogen-bonded 1*H*-1,2,4-diazaphospholes.