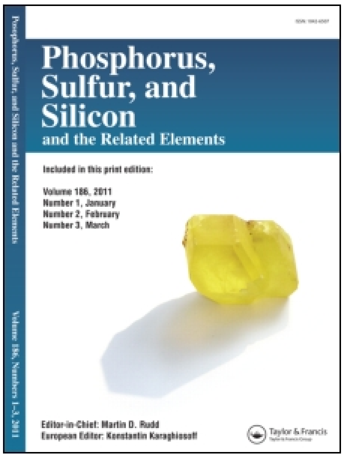

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Zhang, Jing-Lin and Xu, Wei(1990) 'THE CHEMISTRY OF FUSED DICYCLOTRIAZAPHOSPHOLE I. THE SYNTHESIS AND CONFORMATION OF 2-SUBSTITUTED-3-DIALKYLAMINO- 5,6-DISUBSTITUTED THIAZOLO-2,3- DIHYDRO-1,2,4,3-TRIAZAPHOSPHOLES', Phosphorus, Sulfur, and Silicon and the Related Elements, 47: 1, 173 — 180

To link to this Article: DOI: 10.1080/10426509008046858

URL: http://dx.doi.org/10.1080/10426509008046858

Phosphorus, Sulfur, and Silicon, 1990, Vol. 47, pp. 173–180
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THE CHEMISTRY OF FUSED DICYCLOTRIAZAPHOSPHOLE

I. THE SYNTHESIS AND CONFORMATION OF 2-SUBSTITUTED-3-DIALKYLAMINO-5,6-DISUBSTITUTED THIAZOLO-2,3-DIHYDRO-1,2,4,3-TRIAZAPHOSPHOLES

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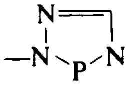
(Received October 8, 1988)

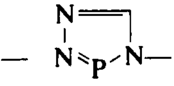
Twelve fused dicyclotriazaphosphole derivatives were synthesized by cyclocondensation reaction of 4,5-disubstituted-2-*N'*-substituted hydrazinothiazoles with $P(NR_2)_3$, $ClP(NR_2)_2$ and Cl_2PNR_2. The conformation of these new compounds were discussed as well on the basis of the spectral data of ^1H, ^{13}C and ^{31}P NMR, MS and of their reaction.

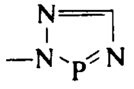
Key words: Cyclocondensation; bis(dialkylamino)chlorophosphine; hydrazinothiazole; tris(dialkylamino)phosphine; conformation; dicyclotriazaphosphole.

INTRODUCTION

With the rapid development of the organophosphorus chemistry, heterocyclic compounds of phosphorus have received considerable attention.[1,2] The monocyclotriazaphosphole (1) has been studied widely.[3–5] Recently the fused tricyclotriazaphosphole (2) has been synthesized in our laboratory.[6,7] However fused dicyclotriazaphosphole derivatives and their properties have never been described. Here we report the synthesis and some properties of these new compounds.


(1a)


(1b)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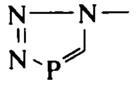
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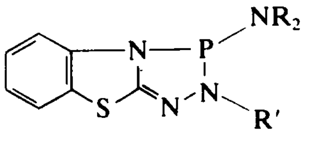
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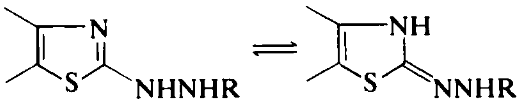
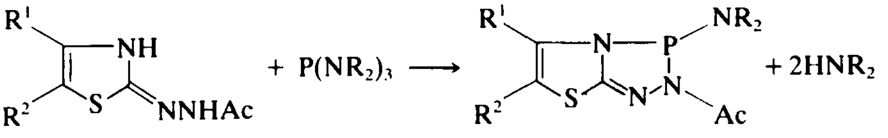
RESULTS AND DISCUSSION

The Synthesis and Spectral Data of Compounds (I) *and* (II)

Tautomer existed commonly in the derivatives of 2-hydrazinothiazole.[8] This character is very useful to synthesize triazaphosphole derivatives. 2-Aceto-3-*N*,*N*-



dialkylamino-5,6-disubstituted thiazolo-[2,3-d]-2,3-dihydro-1,2,4,3-triazaphospholes (**I**) were obtained easily from the reaction of N^2-aceto-2-hydrazinothiazole with tris(dialkylamino)phosphines as shown in following equation.



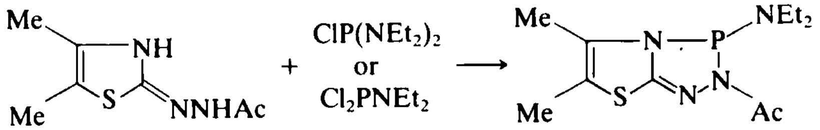
(1)

(**I**)

Ia–d: $R^1 = R^2 = Me$; R = Me, Et, *n*-Pr, *n*-Bu.
Ie–h: $R^1 = Ph$, $R^2 = H$; R = Me, Et, *n*-Pr, *n*-Bu.

The products (**I**) can be purified by preparative TLC with satisfactory yield.

When the dialkylamino group in tris(dialkylamino)phosphines was replaced stepwise by chlorine, the same results were given as reaction (1), but the reaction becomes easier subsequently than latter.



(2)

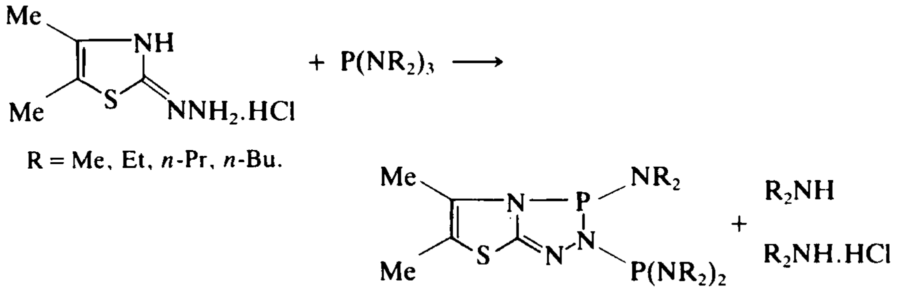
(**Ib**)

Reaction (1) carried out at temperature higher than 80°C, but the reaction (2) began at room temperature and completed at 60°C with bis(diethylamino)chlorophosphine and occured at 0°C and went to completion at 40°C with dichlorodiethylaminophosphine. This shows that P—Cl bond more active than P—NR_2 bond in this reaction and the order of ease of cyclocondensation ability should be as following:

$$Cl_2PNR_2 > ClP(NR_2)_2 > P(NR_2)_3$$

I can be easily resolved in $CHCl_3$, CH_2Cl_2 and THF and have considerable stability at room temperature.

Another fused dicyclic triazaphosphole derivatives could be obtained by the similar cyclocondensation of hydrochloride salt of 4,5-dimethyl-2-hydrazinothiazole with tris(dialkylamino)phosphines.



(3)

R = Me, Et, *n*-Pr, *n*-Bu.

(**II**)

TABLE I

The physical properties and elements analysis data of **I** and **II**

	Substitute							Elements analysis[c]	
No.	R^1	R^2	R	Molecular formula (Mol. Wt.)	Yield (%)[a]	Physical properties	m.p.[b] (°C)	$P_{calc.}$ (%)	P_{found} (%)
Ia	Me	Me	Me	$C_9H_{15}N_4OPS$ (258)[d]	84.3	White Crystal	75.5–76	12.01	11.98
Ib	Me	Me	Et	$C_{11}H_{19}N_4$(OPS (286)	80.6	White Crystal	52–53	10.80	10.62
Ic	Me	Me	*n*-Pr	$C_{13}H_{23}N_4OPS$ (314)	86.2	Yellowish Crystal	31–32	9.87	9.72
Id	Me	Me	*n*-Bu	$C_{15}H_{27}N_4OPS$ (342)	85.7	Yellow Sticky Liquid	—	9.06	8.89
Ie	Ph	H	Me	$C_{13}H_{15}N_4OPS$ (306)	90.1	White Crystal	107–108	10.13	9.93
If	Ph	H	Et	$C_{15}H_{19}N_4OPS$ (334)	87.7	White Crystal	83–83.5	9.28	9.19
Ig	Ph	H	*n*-Pr	$C_{17}H_{23}N_4OPS$ (362)	90.8	White Crystal	60–60.5	8.56	8.37
Ih	Ph	H	*n*-Bu	$C_{19}H_{23}N_4OPS$ (390)	90.3	Yellow Sticky Liquid	—	7.95	7.79
IIa	Me	Me	Me	$C_{11}H_{24}N_6P_2S$ (334)	79	Yellow Sticky Liquid	—	18.56	18.37
IIb	Me	Me	Et	$C_{17}H_{36}N_6P_2S$ (418)[d]	87	Yellow Sticky Liquid	—	14.83	14.69
IIc	Me	Me	*n*-Pr	$C_{23}H_{48}N_6P_2S$ (502)	88	Yellow Sticky Liquid	—	12.35	12.17
IId	Me	Me	*n*-Bu	$C_{29}H_{60}N_6P_2S$ (586)	82	Yellow Sticky Liquid	—	10.58	10.37

[a] Yield of purified products.

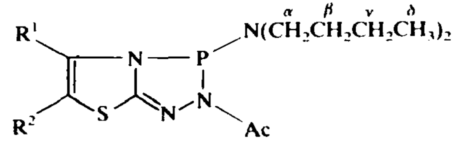
[b] m.p. is uncorrect.

[c] The maximum analysis deriation of carbon and hydrogen are C ± 0.31, H ± 0.08.

[d] MS of **Ia**: $m/e = 258$ (88.7%, M^+), $m/e = 214$ (9.7%, $-NMe_2$); MS of **IIb**: $m/e = 418$ (48.1%, M^+), $m/e = 175$ (100%, $^+P(NEt_2)_2$).

TABLE II

The ^1H, ^{13}C and ^{31}P NMR data of **I**



No.	^1H NMR (ppm)				^{13}C NMR (ppm)				^{31}P NMR (ppm)
	Hα	Hβ	Hν	Hδ	Cα	Cβ	Cν	Cδ	
Ia	2.6(d)6H $^3J_{PH} = 8.8$ Hz	—	—	—	36.4(d) $^2J_{PC} = 18.9$ Hz	—	—	—	108.0
Ib	3.0(d)4H $^3J_{PH} = 7.0$ Hz	1.1(t)6H			39.7(d) $^2J_{PC} = 19.5$ Hz	11.2	—	—	107.4
Ic	2.9(d)4H $^3J_{PH} = 7.0$ Hz	1.5(m)4H	0.9(t)6H	—	47.0(d) $^2J_{PC} = 19.9$ Hz	22.0	10.9	—	107.5
Id	2.9(d)4H $^3J_{PH} = 7.0$ Hz	1.4(m)4H	1.2(m)4H	1.0(t)6H	46.1(d) $^2J_{PC} = 19.9$ Hz	30.9	20.8	11.0	107.5
Ie	2.6(d)6H $^3J_{PH} = 8.8$ Hz	—	—	—	36.3(d) $^2J_{PC} = 19.9$ Hz	—	—	—	110.3
If	3.0(d)4H $^3J_{PH} = 6.9$ Hz	1.1(t)6H	—	—	42.0(d) $^2J_{PC} = 19.7$ Hz	11.0	—	—	110.0
Ig	2.9(d)4H $^3J_{PH} = 7.0$ Hz	1.9(m)4H	1.0(t)6H	—	43.2(d) $^2J_{PC} = 19.4$ Hz	18.7	11.3	—	109.7
Ih	2.8(d)4H $^3J_{PH} = 7.0$ Hz	1.6(m)4H	1.4(m)4H	1.0(t)6H	45.0(d) $^2J_{PC} = 20.0$ Hz	30.0	19.9	11.7	109.7

* ^1H, ^{13}C and ^{31}P NMR spectra were taken on the Varian XL-200 in $CDCl_3$ at room temperature. NMR signals of quaternary carbon, carbon in R^1, R^2 and methyl carbon in aceto group were omitted from this Table, but they are all in agreement with their structure.

II are more sensitive to moisture than **I** and decomposed in acidic conditions. Fortunately, they can be purified by TLC under basic condition and stored in nitrogen atmosphere. The difference in stability of **II** and **I** is probably related to the substitution of electron-with-drawing aceto group in **I** for electron-donating —$P(NR_2)_2$ groups in **II**. The details will be discussed in other paper.

The Structure and Conformation of Compounds (II)

Two phosphorus nuclei of **II** give rise to two signals in ${}^{31}P$ NMR spectra. From the decoupled spectra of **II** (see Table III), it is easy to recognize that signals in high field (77.8–80.0 ppm) can be attributed to cyclic phosphorus nucleus and the signals of exo-cyclic phosphorus nucleus appear in the low field (104.6–113.3 ppm). This can be supported by literature[6,9] and non-decoupled spectrum of **IIb**, in which the signal in higher field is split into double quintet peaks by four α-H attached on adjacent nitrogen atom, and that in lower field is split into double ninefold peaks owing to eight α-H on nitrogen atoms.

R. Keat, R. J. Cross and H. J. Chen have pointed out that the bridging nitrogen atom has a planar distribution of bonds for acyclic P–N–P skeleton and there is presumably d_π–p_π overlap between phosphorus and nitrogen. It is now generally recognized that two limiting conformation C_{2v}(cis) and C_s(trans) related to lone pair electron on two phosphorus atoms of diphosphines are most likely and the C_{2v}(cis) conformation is associated with a large positive PNP spin coupling at the range above 200 Hz, whereas for C_s(trans) conformation ${}^2J_{PP}$ are known to be relatively small, 18–25 Hz.[10] Since a large ${}^2J_{PP}$ in the range of 195.6–239.3 Hz, **II** prefer C_{2v} conformation. The coupling constant of PNP also increase with increasing size of the phosphorus substituent in the series of Me, Et, *n*-Pr, *n*-Bu. The sharp of peaks in ${}^{31}P$ NMR spectra of **II** shows P–N–P bonds can not rotate freely around their bonds.

As indicated by ${}^1H$ and ${}^{13}C$ NMR spectra in Table IV, the six R groups on three nitrogen atoms of **II** can be devided into three classes (R, R^1, R^2). α-C and α-H in each class couple with phosphorus nuclei in different degrees and the values of ${}^2J_{PC}$ and ${}^3J_{PH}$ obey the following sequence:

$$ {}^2J_{P_{cyc}C} \gg {}^2J_{P_{exo}C^1} > {}^2J_{P_{exo}C^2} $$

$$ {}^3J_{P_{cyc}H} \gg {}^3J_{P_{exo}H^1} > {}^3J_{P_{exo}H^2} $$

The P_{cyc}–N_{cyc} stretching absorption in IR spectra of **I** and **II** appears as a strong band with maximum absorption at approximately 1189–1245 cm^{-1}. The $\nu(P_{exo}$–

TABLE III

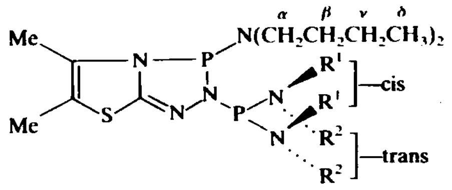
${}^{31}P$ NMR data of **II**

No. (R)	**IIa** (R = Me)	**IIb** (R = Et)	**IIc** (R = *n*-Pr)	**IId** (R = *n*-Bu)
P_{cyc} (ppm)	77.8(d)	77.9(d)	78.7(d)	80.0(d)
P_{exo} (ppm)	112.1(d)	104.6(d)	106.5(d)	106.8(d)
${}^2J_{PNP}$ (Hz)	195.6	217.8	229.5	239.3

* ${}^{31}P$ NMR spectra were taken on the Varian XL-200 in $CDCl_3$ at room temperature.

TABLE IV

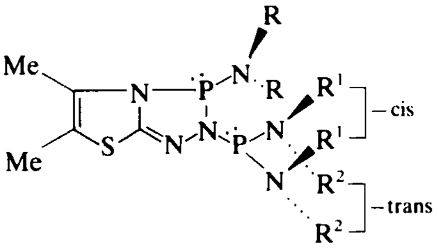
^1H, ^{13}C NMR spectra data of **II**



R	^1H NMR (ppm)				^{13}C NMR (ppm)			
	Hα	Hβ	Hν	Hδ	Cα	Cβ	Cν	Cδ
Me	R 1.8(d)6H $^3J_{PH} = 8.6$ Hz	—	—	—	36.6(d) $^2J_{PC} = 15.7$ Hz	—	—	—
	R^1 1.9(d)6H $^3J_{PH} = 9.5$ Hz	—	—	—	37.7(d) $^2J_{PC} = 18.9$ Hz	—	—	—
	R^2 2.0(d)6H $^3J_{PH} = 9.0$ Hz	—	—	—	38.5(d) $^2J_{PC} = 18.7$ Hz	—	—	—
Et	R 2.8–3.2(m)	1.0(t)6H	—	—	39.9(d) $^2J_{PC} = 13.4$ Hz	14.3	—	—
	R^1 2.8–3.2(m)	1.1(t)6H	—	—	40.0(d) $^2J_{PC} = 19.5$ Hz	14.5	—	—
	R^2 2.8–3.2(m)	1.1(t)6H	—	—	40.2(d) $^2J_{PC} = 19.3$ Hz	14.7	—	—
n-Pr	R 2.7–3.5(m)	1.1–2.8(m)	0.7–1.0(m)	—	48.6(d) $^2J_{PC} = 16.2$ Hz	20.9	10.5	—
	R^1 2.7–3.5(m)	1.1–2.8(m)	0.7–1.0(m)	—	49.0(d) $^2J_{PC} = 19.1$ Hz	21.9	11.1	—
	R^2 2.7–3.5(m)	1.1–2.8(m)	0.7–1.0(m)	—	49.4(d) $^2J_{PC} = 19.3$ Hz	22.1	11.4	—
n-Bu	R 2.7–3.3(m)	1.0–1.7(m)	1.0–1.7(m)	0.8–1.0(m)	46.3(d) $^2J_{PC} = 16.1$ Hz	29.4	19.2	12.9
	R^1 2.7–3.3(m)	1.0–1.7(m)	1.0–1.7(m)	0.8–1.0(m)	47.1(d) $^2J_{PC} = 19.1$ Hz	30.0	20.0	12.0
	R^2 2.7–3.3(m)	1.0–1.7(m)	1.0–1.7(m)	0.8–1.0(m)	47.3(d) $^2J_{PC} = 19.0$ Hz	30.3	20.7	12.1

• ^1H and ^{13}C NMR spectra were taken on the Varian XL-200 in $CDCl_3$ at room temperature. NMR signals of quaternary carbon, carbon in two methyl groups were omitted from this Table. In ^1H NMR spectra the areas of integration are proportional to the number of hydrogen in given structure. The chemical shifts of α-H for **IIb**, **IIc** and **IId** appeared in a very narrow region and strongly overlapped each other. It is difficult to recognize them in detail. It did so for β-H (1.1–2.8 ppm), ν-H(0.7–1.7 ppm) and δ-H(0.8–1.0 ppm) for **IIc** and **IId**.

N_{cyc}) is at approximately 1140–1177 cm^{-1}, whereas P_{cyc}–N_{exo} of **I, II** and P_{exo}–N_{exo} of **II** stretching absorption occurs at lower frequency with maximum absorption at 924–951 cm^{-1} and 904–909 cm^{-1} respectively. This means that the P_{cyc}–N_{cyc} and P_{exo}–N_{cyc} bonds are characterized by some P═N double bond. Only P_{cyc}–N_{exo} and P_{exo}–N_{exo} bonds remain as single.[11] It shows that there is a conjugation interaction between P_{cyc} and N_{cyc} as in the case of fused tricyclic triazaphospholes.[12] This is the reason for $^2J_{P_{cyc}C} \gg {}^2J_{P_{exo}C}$[1,2]. Normally a large coupling constant will occur if the lone pair electrons on phosphorus are in cis conformation with R group.[13] So we assume that the R^1 group, characterized by a strong J value, is located at cis position to the lone pair electrons on the exo-cyclic phosphorus and R^2 with smaller J is located at the trans-position, as drawn out in figure.



EXPERIMENTS

The Synthesis of **I**. 10 ml xylene, 0.5 g tris(diethylamino)phosphine and 0.5 g N-aceto-2-hydrazinothiazole are placed in a round bottom flask. The mixture is heated at 80°C and 120 torr under nitrogen atmosphere for 1.5 hrs. Then the solvent is evaporated in vacuo and the residual crude product is purified by preparative TLC on silicon gel using ether, petroleum ether (1:4) as eluent. 0.6 g pure **Ib** was obtained in the yield of 80.6%.

The similar method can be used to synthesis **Ia** and **Ic–Ih**.

The Synthesis of **II**. Under nitrogen atmosphere 0.5 g dried hydrochloride salt of 2-hydrazino-4,5-dimethylthiazole and 10 ml xylene was placed in a flask. 3 ml $P(NEt_2)_3$ was added when the mixture was heated to 70°C. The mixture was stirred under reduced pressure and heated to 90–95°C for 0.5 hrs. The clear crude product was separated and purified by TLC on silicon gel using triethylamine and petroleum ether (1:5) as eluent. 0.90 g yellow sticky liquid with foul smell of **IIb** was obtained in the yield of 87%.

In the same way, **IIa**, **IIc** and **IId** also can be obtained, but the temperature should be controlled at 80°C, 100°C and 105°C respectively.

ACKNOWLEDGEMENT

We gratefully acknowledge support for this work by the National Science Foundation of China. The author also would like to express thanks to The Analysis Centre of Huazhong Normal University and their colleagues for IR, NMR and elements analysis.

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