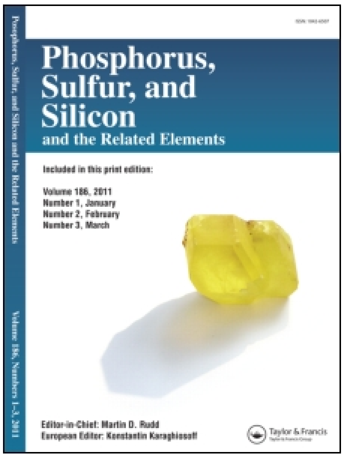

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A NEW SYSTEM EXHIBITING A HIGH BARRIER TO ROTATION ABOUT THE P—N BOND. SYNTHESES AND SPECTRAL STUDIES OF 1,3,2-DIAZAPHOSPHETIDIN-4-ONE DERIVATIVES

Xiao-Bo[a]; Jing-Lin Zhang[b]
[a] Institute of Chemistry, Academia Sinica, Beijing, China [b] Institute of Organic Synthesis, Huazhong Normal University, Wuhan, Hubei, China

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A NEW SYSTEM EXHIBITING A HIGH BARRIER TO ROTATION ABOUT THE P—N BOND. SYNTHESES AND SPECTRAL STUDIES OF 1,3,2-DIAZAPHOSPHETIDIN-4-ONE DERIVATIVES

XIAO-BO MA[a*] and JING-LIN ZHANG[b]
[a] *Institute of Chemistry, Academia Sinica, Beijing, China*
[b] *Institute of Organic Synthesis, Huazhong Normal University, Wuhan, Hubei, China*

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1,3,2-Diazaphosphetidin-4-one derivatives were synthesized. Their ^1H NMR signals at ambient temperature displayed a broad doublet which eventually coalesced before becoming sharp upon warming, and the ^{13}C NMR spectra also showed that the α- and β-carbons of the dialkylamino group were non-equivalent. The phenomena were ascribed to restricted rotation about the exocyclic P—N bond.

Key words: Restricted rotation; coalescence temperature; phosphorus and nitrogen inversional barrier; 1,3,2-diazaphosphetidin-4-one; constraint of four-membered ring.

For a long time, it has been known that the bonding between phosphorus and nitrogen in some of the phosphorus amide compounds appears to have significant π character. A strong evidence for the existence of π system was the restricted rotation about P—N bond observed from the variable-temperature proton and fluorine nuclear magnetic resonance.[1] For example, chloro(dimethylamino)phenylphosphine, $PPhCl(NMe_2)$, was one of the acyclic aminophosphines investigated most extensively. Its ^1H NMR spectrum displayed broad and coalesced signals in the methyl region when the temperature was lowered. The coalescence temperature, T_c, was $-50°C$, at which the free energy of activation ($\Delta G^{\ddagger}_{T_c}$) for rotation about the P—N bond was $10.9\,\mathrm{kcal\,mol^{-1}}$ (from Eyring equation).[2–4] Our continued interest in the chemistry of diaza- and triazaphosphole[5] prompted us to synthesize the derivatives of 1,3,2-diazaphosphetidin-4-one, which have been reported.[6–8] Here we wish to report the reaction of urea derivatives containing at least one aryl group with tris(dialkylamino)phosphines without solvent at 100–130°C under a nitrogen atmosphere of 20–70 torr. About 60–75% yields of product **1** could be obtained (Table I).

The ^1H NMR spectrum of compounds **1** in $CDCl_3$ at ambient temperature

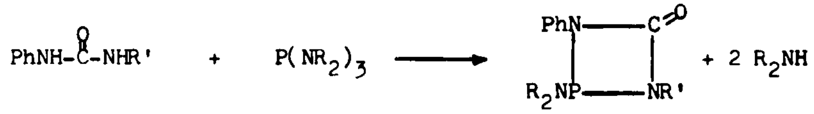

TABLE I

2-(Dialkylamino)-1-phenyl-3-alkyl(or aryl)-1,3,2-diazaphosphetidin-4-one prepared[a]

Entry	*R*	*R'*	Yield[b] %	Temp. °C	N_2 Press.[c] torr	Time h	mp °C
1a	Me	Ph	70	100	70	3	110–111
1b	Et	Ph	69	105	45	1.5	89–90
1c	*n*-Pr	Ph	66	110	40	2	106–107
1d	*n*-Bu	Ph	61	120	25	2	liquid
1e	Et	*p*-MeC_6H_4	69	105	50	1.5	80–81
1f	Et	$PhCH_2$	71	120	20	1.5	liquid
1g	Et	Me_2CH	75	132	50	1	
1h	Et	*p*-$EtOC_6H_4$	76	130	20	1	
1i	*n*-Bu	*p*-MeC_6H_4	76	118	10	2	

[a] All compounds gave satisfactory MS spectral data and microanalysis.

[b] Yield of isolated products.

[c] The reaction proceeded under a nitrogen atmosphere of reduced pressure to favour the removal of the gaseous dialkylamine and to isolate from oxygen.

displayed a broad doublet in the region of the aliphatic protons of dialkylamino group (Table II). As the temperature was raised, the broad doublet eventually coalesced and displayed the normal ^1H NMR signals, as depicted by (a) for compound **1a** and (b) for compound **1b** in Figure 1. The phenomena arose from the barriers related to the possible conformational changes comprising rotation around the P—N bonds and pyramidal inversion at both nitrogen and phosphorus. Table II shows that the free energies of activation fall in the range 14–16 kcal mol^{-1}, much less than the free energy of activation for phosphorus pyramidal inversion in simple tertiary phosphines (~30 kcal mol^{-1}).[9] Therefore, phosphorus inversion is not expected to occur throughout the temperature range here.[3,10] In addition, an increase of activation energy was observed by Cowley and his coworkers when bulkier groups were present at nitrogen, which indicated that the barriers related to rotation about the exocyclic P—N bonds, rather than to inversion at the exocyclic nitrogen atom.[3,11] And the nitrogen inversional barrier in aminophosphines was small and nitrogen atom was inverting rapidly on the NMR time scale throughout the temperature ranges used here.[3,10,11] Thus, the barriers which relate to the rotation about the exocyclic P—N bond slow the motions within the molecule on the NMR time scale and the energies can be exchanged easily between spin nuclei. The spin–spin relaxation time of the protons is short, leading to the broadening effects of the ^1H NMR spectra.

Another interesting feature of ^1H NMR spectra of compounds **1** is that two PNCH couplings for the dialkylamino group were observed at ambient temperature except for compounds **1e**, **1g** and **1i**. And ^{13}C NMR spectra also gave two couplings of α- and β-carbons to phosphorus (Table III). It is clearly demonstrated that the two alkyl groups are non-equivalent and the preferred conformation is one in which the alkyl groups lie in, or close to the plane passing through the phosphorus and carbon of carbonyl group and perpendicular to the 1,3,2-diazaphosphetidin-4-one ring to minimize the steric interactions (Figure 2).

TABLE II

^{1}H NMR and other physical data from compounds **1**

Compd	T_c (K)	$\Delta G^{\ddagger a}_{T_c}$ kcal mol^{-1}	^{1}H NMR^b δ [*ppm*]	$\Delta\nu_{CH_2}$(Hz)^b
1a	306	14.6	2.5–3.0 (2b, 6H, 13.6, 11.8); 7.0–7.5 (m, 10H)	105
1b	308	14.8	0.8–1.5 (2b, 6H); 2.8–3.6 (2b, 4H, 9.4, 6.6); 7.0–7.5 (m, 10H)	93
1c	321	15.4	0.6–1.1 (2b, 6H); 1.2–1.9 (2b, 4H); 2.7–3.5 (2b, 4H, 10.5, 5.5); 7.0–8.0 (m, 10H)	96
1d	324	15.5	0.6–2.0 (m, brd, 14H); 2.6–3.6 (2b, 4H, 9.8, 6.3); 7.0–7.9 (m, 10H)	93
1e	331	15.9	0.8–1.4 (2b, 6H); 2.9–3.6 (2b, 4H); 2.3 (s, 3H); 6.9–7.8 (m, 9H)	105
1f	311	14.8	0.6–1.4 (2b, 6H); 2.6–3.3 (2b, 4H, 11.9, 8.6); 4.4 (d, 2H, 10.3); 6.9–7.6 (m, 10H)	114
1g	333	16.1	0.8–1.3 (2b, 6H); 1.3–1.7 (2d, 6H); 2.8–3.5 (2b, 4H); 3.8–4.2 (m, 1H, 9.7); 6.9–7.6(m, 5H)	90
1h	326	15.6	0.6–1.3 (2b, 6H); 1.4 (t, 3H); 2.7–3.5 (2b, 4H, 8.7, 5.2); 3.7–4.0 (m, 2H); 6.6–7.5 (m, 9H)	108
1i	339	16.3	0.6–2.1 (m, brd, 14H); 2.6–3.5 (2b, 4H); 2.3 (s, 3H); 6.9–7.7 (m, 9H)	99

[a] Calculated from the Eyring equation assuming a transmission coefficient of unity and that $k_c = \pi\Delta\nu/2^{1/2}$.

[b] Recorded relative to Me_3Si. The two coupling constants of hydrogen as split by the phosphorus atom are given in hertz in parentheses. s: singlet; t: triplet; 2b: broad doublet; 2d: two doublets; m: multiplet. $\Delta\nu_{CH_2}$ is the difference in chemical shift between the resolved NCH_2 (or NCH_3) signals in the absence of exchange.

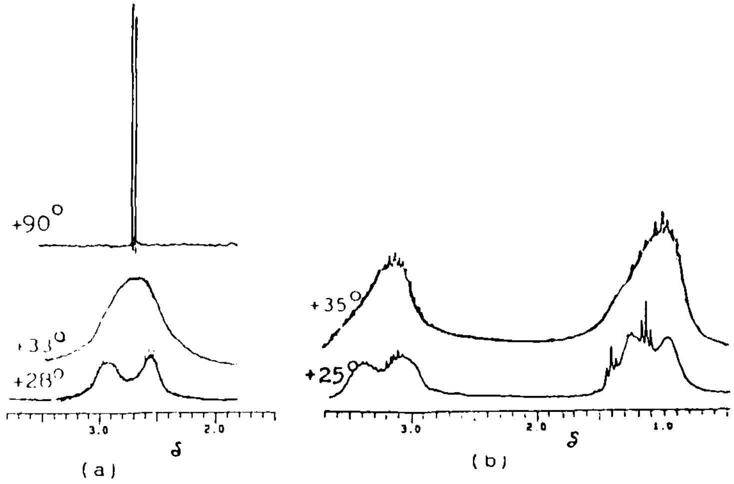

FIGURE 1 ^{1}H NMR spectra of (a) methyl region of compound **1a**, (b) ethyl region of compound **1b**.

TABLE III

^{31}P, ^{13}C NMR and IR spectral data of compounds **1**

	^{31}P NMR[a]	^{13}C NMR δ [ppm][b]			IR ν[cm^{-1}][c]	
Compd	δ[ppm]	Ç=O	α-Ç	β-Ç	C=O	P—N
1a	85.9	152.3 (11.8)	37.8 (7.6) 32.3 (18.0)		1742	1232 1192 977
1b	82.5	151.9 (12.2)	43.1 (8.9) 36.2 (17.1)	16.2 (6.1) 13.2 (11.0)	1740	1202 1176 996
1c	83.0	152.6 (11.5)	43.5 (7.5) 49.1 (17.5)	22.6 (6.5) 19.5 (10.8)	1741	1239 1173 996
1d	83.3	151.6 (11.9)	46.8 (7.8) 40.5 (15.5)	30.9 (7.1) 27.5 (11.5)	1742	1231 1175 996
1e	82.0	152.4 (11.8)	44.5 (9.8) 39.0 (18.0)	15.7 (6.4) 12.5 (10.6)	1734	1203 1176 996
1f	83.5	153.3 (9.5)	44.5 (7.3) 38.6 (17.8)	14.6 (6.5) 11.5 (11.0)	1732	1202 1177 942
1g	77.8	152.8 (11.6)	43.5 (7.3) 37.4 (17.3)	13.5 (6.9) 11.6 (10.5)	1727	1202 1178 978
1h	82.3	154.7 (11.6)	42.5 (7.6) 37.5 (16.8)	15.2 (6.4) 12.6 (10.8)	1738	1202 1176 996
1i	82.4	151.9 (11.9)	47.1 (8.2) 40.6 (16.2)	31.8 (7.2) 26.8 (11.8)	1736	1202 1176 996

[a] ^{31}P NMR spectra were measured using 85% H_3PO_4 as external reference.

[b] ^{13}C NMR spectra were measured in $CDCl_3$ relative to internal Me_4Si. The data are only given for α- and β-C of dialkylamino group attached to phosphorus atom. The coupling constant of carbon as split by the phosphorus is given in hertz in parentheses.

[c] Recorded as KBr plates or film on NaCl on a Perkin-Elmer 983 spectrometer.

Thus, the nitrogen lone pair lies orthogonal to the phosphorus lone pair,[3] as indicated by X-ray analysis of the similar structure.[7] The alkyl group cis to the phosphorus lone pair will have a relatively large PNCH coupling and the alkyl group trans to it will have a small one.[8,11,12] Compounds **1e**, **1g** and **1i** with large size of the cyclic nitrogen substituent possess higher coalescence temperature so that the split signals weren't observed at ambient temperature.

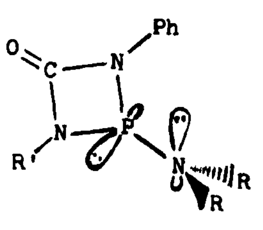

FIGURE 2

The IR spectra of compounds **1** showed several P—N bond absorptions. As compared to the normal values of 1100–930 cm^{-1}, the extremely high absorption at *ca.* 1200 cm^{-1} was assigned to the exocyclic P—N bond vibration, in addition, there were two slightly higher ring P—N bond vibrations at 1176 and 996 cm^{-1}. It is obvious that the exocyclic P—N bond possesses the characteristics of double bond P=N, and the ring P—N bonds also have strong $p-\pi$ interaction.[13] Another phenomenon is that the carbonyl absorptions of these compounds were observed between 1727–1742 cm^{-1}, while for the disubstituted urea it was at about 1660 cm^{-1}. This shift of carbonyl absorption to higher frequency could be attributed to the strain in the small ring system of **1**.[14] The free energies of activation at T_c were higher than those of the acyclic aminophosphines by *ca.* 4 kcal mol^{-1} (Table II),[3] which could be ascribed to the strengthened $\mathrm{p}\pi-\mathrm{d}\pi$ interaction of exocyclic P—N bond by electron-withdrawing carbonyl and the great steric constraint of the four-membered ring.[11]

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