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^{1}H, ^{13}C and ^{31}P NMR Studies of 2-(Substituted Phenoxy) 2,3-Dihydro-1H-Naphtho- [1,8-de]-1,3,2-Diazaphosphorine-2-oxides

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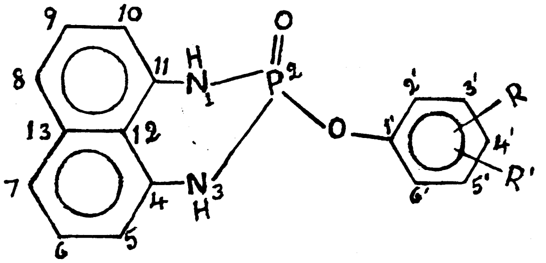
NMR data for title compounds show that diazaphosphorine 2-oxide system does not exert significant influence on the aryloxy protons. The P–C coupling constants provide support for the half chair conformation of the diazaphosphorine ring with equatorial orientation of the aryloxy group. The ^{31}P signals appeared over a wide region –6.35 to –5.27 ppm showing that the ^{31}P chemical shifts are sensitive to subtle differences in the structure of the molecules and stereo electronic environment. The NH proton signal appeared as a doublet in downfield at δ 8.1–8.7 ($^{2}J_{P-N-H} = 5.4$–6.0 Hz) due to its coupling with phosphorus.

INTRODUCTION

In connection with studies on organophosphorus insecticides and pesticides, the title compounds (1–11) are synthesised[1] and their ^{1}H, ^{13}C and ^{31}P NMR spectral characteristics are studied.



Compound No.	R	R'	Compound No.	R	R'
1	H	H	7	3'—CH_3	4'—CH_3
2	2'—CH_3	H	8	3'—CH_3	5'—CH_3
3	3'—CH_3	H	9	2'—Cl	H
4	4'—CH_3	H	10	4'—Cl	H
5	2'—CH_3	3'—CH_3	11	2'—Cl	4'—Cl
6	2'—CH_3	6'—CH_3			

RESULTS AND DISCUSSION

^{1}H NMR spectra

The NH proton signals in all the compounds (Tables 1 and 2) appeared as doublets at δ 8.2–8.6 with $^{2}J_{P-N-H} = 5.4–6.0$ Hz due to its coupling with phosphorus. However, for 4 and 10 its value is shifted to 6.4 ppm which may be due to the change of NMR solvent in their recording (Table 1). Hydrogen bonding with the oxygen of P=O and the deshielding effect of aryloxy phosphoryl group (Ar–O–P=O) are obviously the contributing factors for the downfield shift of the NH proton.

TABLE 1

NAPHTHYL, NH PROTONS[b] AND ^{31}P CHEMICAL SHIFTS[a] OF 1–11

Compound	5,10–H H_a	6,9–H H_b	7,8–H H_c	NH	^{31}P
1	6.73 (d, 8.4)	7.15 (dd, 8.4 & 8.0)	7.23 (d, 8.0)	8.19 (d, 5.8)	—
2	6.74 (d, 8.6)	7.07 (dd, 7.7 & 8.6)	7.25 (d, 7.7)	8.69 (d, 5.7)	–5.4
4	6.65 (d, 7.1)	7.25 (dd, 8.3 & 7.1)	7.35 (d, 8.3)	6.40 (d, 6.0)	–5.3
5	6.87 (d, 7.5)	6.96 (dd, 7.5 & 7.9)	7.11 (d, 7.9)	8.49 (d, 5.7)	—
7	6.72 (d, 7.9)	6.82 (d, 8.0)	6.94 (d, 8.4)	8.49 (d, 5.7)	–6.2
8	6.72 (d, 7.9)	6.82 (dd, 7.9 & 7.5)	7.23 (d, 7.5)	8.13 (d, 5.7)	–6.3
9	6.73 (d, 8.0)	7.18 (dd, 8.0 & 7.8)	4.24 (d, 7.8)	8.65 (d, 5.4)	—
10	6.67 (d, 7.4)	7.28 (dd, 7.4 & 8.1)	7.38 (d, 8.1)	6.37 (d, 5.7)	–5.8
11	—	—	—	—	–5.3

[a] Chemical shifts (δ) in ppm and coupling constants (J) in Hz

[b] Compounds 4 and 10 recorded in $CDCl_3$ and the others in $CDCl_3$ + DMSO – d_6

Though there are six protons in the naphthalene system, only three signals were observed for them because of their symmetrical disposition with respect to diazaphosphorine 2-oxide ring system. The signals of H_5 and H_{10} appeared up field at δ 6.65–6.87 ($J_{H_5-H_6} = 7.1–8.6$ Hz) due to the shielding effect of the NH of the diazaphosphorine ring. The H_6 and H_9 resonated as a doublet of doublet at δ 6.82–7.28, $J_{H_6-H_5} = 7.1–8.6$ Hz; $J_{H_6-H_7} = 7.5–8.4$ Hz. The shifts of H_7 and H_8 appeared downfield at 6.94–7.38 ppm ($J_{H_7-H_6} = 7.5–8.4$ Hz) due to the deshielding effect of diazaphosphorine 2-oxide system.

TABLE 2
PROTON CHEMICAL SHIFTS[a] OF PHENOXY MOIETY OF 1–11

Compound	H_2	H_3	H_4	H_5	H_6	Methyl-H
1		Complex multiplet 6.70–7.39 (m, 5H)				—
2	—	7.04 (d, 7.6)	7.33 (dd, 9.1, 7.6)	6.97 (dd, 7.6, 9.1)	6.73 (d, 7.7)	2.07 (3H)
4		Single signal at 7.29 for 4H				2.18 (3H)
5	—	—	6.72 (d, 8.4)	6.89 (dd, 8.5, 8.4)	6.86 (d, 8.4)	1.97 (3H) 2.18 (3H)
7		Complex multiplet 6.70–7.54 (m, 3H)				2.19 (6H)
8	6.70 (d, 3.2)	—	6.72 (d, 3.2)	—	6.70 (d, 3.2)	2.12 (6H)
9	—	5.98–7.16 (m, 1H)	7.37 (dd, 7.6, 7.4)	6.98–7.16 (m, 1H)	6.75 (d, 8.3)	—
10	7.02 (d, 8.4)	7.15 (d, 8.4)	—	7.15 (d, 8.4)	7.02 (d, 8.4)	—

[a] δ in ppm from TMS and J in Hz.

Aryloxy protons, in 4-methyl compound (4) resonated at δ 7.29 and their integration corresponds to four protons with no splitting of the signal. This shows that all the protons are magnetically equivalent. In 4-chloro derivative (10) $H_{3'}$ and $H_{5'}$ showed one signal at δ 7.15, $J_{H-H} = 8.5$ Hz while $H_{2'}$ and $H_{6'}$ exhibited another single signal at δ 7.02, $J_{H-H} = 8.5$ Hz. This shows that $H_{3'}$, $H_{5'}$ and $H_{2'}$, $H_{6'}$ are magnetically equivalent. Protons of the aryloxy moiety in other compounds resonated in the expected range. Diazaphosphorine 2-oxide moiety does not exert any influence on the aryloxy protons.

^{13}C NMR spectra

The ^{13}C NMR data for a few of the title compounds (3, 4, 7, 9 and 10) are given in Table 3. The carbon shifts are assigned based on the additivity principle, observed coupling constants, signal intensities and SFORD spectra. The naphthodiazaphosphorine moiety of the title compounds exhibited only six signals for naphthalene carbons because of their symmetrical disposition with respect to diazaphosphorine ring. The carbons, C_4 and C_{11}, which are connected to phosphorus through NH, resonated at δ 112.7 with $^2J_{P-N-C_4 \& C_{11}} = 7.8–8.1$ Hz. The signal around 108.0 ppm, $^3J_{P-N-C_5 \& C_{10}} = 10.6–11.4$ Hz is assigned to C_5 and C_{10}. C_{12} and C_{13} bridge carbons resonated at δ 130.5 and 135.7–137.4 respectively and the difference in their chemical shifts may be attributed to the variation of shielding effect of NH.

The ^{13}C chemical shifts of aryloxy moiety are agreeing well with the reported[2] values. However, in 7, the two *ortho* methyl carbon shifts are observed up field by about 3 ppm which is to be attributed to γ-effect[3].

TABLE 3

^{13}C CHEMICAL SHIFTS[a] OF 3, 4, 7, 9 AND 10

Compound	C-4 & C-11	C-5 & C-10	C-6 & C-9	C-7 & C-8	C-12	C-13	C-1′	C-2′	C-3	C-4	C-5′	C-6′	CH_3
3	—	108.6 (d, J = 11.3)	125.9	118.7	—	137.4	—	121.7 (d, J = 3.7)	134.2	125.9	128.5	118.7	21.2
4	112.8 (d, J = 7.8)	107.6 (d, J = 10.6)	125.6	117.8	130.4	135.7	148.2 (d, J = 8.1)	121.7 (d, J = 3.7)	128.4	134.2	128.4	121.7 (d, J = 3.7)	20.6
7	112.8 (d, J = 7.9)	107.6 (d, J = 10.8)	125.3	117.7	130.6	135.7	148.7 (d, J = 7.3)	121.1 (d, J = 4.5)	138.2	133.6	130.6	117.2 (d, J = 4.4)	16.9
9	112.8 (d, J = 8.1)	107.8 (d, J = 11.2)	125.3	117.9	130.6	136.8	145.4 (d, J = 7.8)	130.6	128.4	126.0	123.9	121.2	—
10	112.6 (d, J = 8.0)	108.6 (d, J = 11.4)	125.9	118.7	130.8	137.4	148.5 (d, J = 9.3)	121.6 (d, J = 5.5)	128.5	130.8	128.5	121.6 (d, J = 5.5)	—

[a] δ in ppm and J in Hz.

$^3J_{P-O-C-C_5 \& C_{10}}$ with large coupling constants (10 Hz) suggests that C_5 and C_{10} carbon atoms are spacially close to phosphorus[4]. The coupling constants for $^2J_{P-O-C_{1'}}$, and $^3J_{P-O-C_{1'}-C_2 \& C_{6'}}$ are concurring with those of equatorially oriented P–O–Ar groups[5] showing the diazaphosphorine ring has probably half chair conformation with phosphorus atom projecting upwards and the O–Ar group orienting equatorially.

^{31}P NMR spectra

^{31}P Chemical shifts of these compounds (Table 1) appeared in the region –6.3 to –5.3 ppm. 3,4 and 3,5-dimethyl compounds (7 & 8) showed their ^{31}P resonances up field by 1 ppm due to the electron releasing effect of the two methyl groups which increase electron density on phosphorus, thereby increasing shielding on it. The above data reveal that phosphorus resonances are very sensitive to subtle difference in its stereo electronic environment.

EXPERIMENTAL

The title compounds are prepared according to the procedure reported[1]. ^{1}H and ^{13}C NMR spectra were recorded on Varian XLAA 300 spectrometer in a mixture of $CDCl_3$ and DMSO–d_6 solutions containing TMS as internal standard. ^{31}P NMR data have been taken on Varian VXR 300 spectrometer using 85% H_3PO_4 as external standard.

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