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Reference Data

Synthesis, ^{1}H, ^{13}C and ^{31}P NMR Spectral Studies of novel 2-Aryloxy/Cyclicamino- 3-(4-methylphenyl)- 1*H*- naphth[1,2-*e*] [1,3,2] oxazaphosphorine 2-oxides/sulphides and ^{13}C NMR Data for some 4-substituted-dinaphtho dioxaphosphepin 4-oxides/sulphides.

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The syntheses, ^{1}H, ^{13}C and ^{31}P NMR chemical shifts and ^{13}C-^{31}P coupling constants of 2-aryloxy/cyclicamino-2,3-dihydro-3-(4-methylphenyl)-1*H*-naphth [1,2-*e*] [1,3,2]oxazaphosphorine 2-oxides/sulphides and the ^{13}C NMR data for 4-substituted-dinaphtho [2,1-*d*:1′,2′-*f*] [1,3,2] dioxaphosphepin 4-oxides/sulphides are reported.

KEY WORDS ^{1}H, ^{13}C and ^{31}P NMR chemical shifts 2-aryloxy-3-(4-methylphenyl)-1*H*-naphth [1,2-*e*][1,3,2] oxazaphosphorine, 2-oxides/sulphides 4-substituted-dinaphtho[2,1-*d*:1′,2′,-*f*] [1,3,2]dioxaphosphepin 4-oxides/sulphides

INTRODUCTION

Naphthoxazaphosphorine 2-oxides/ sulphides and dinaphtho dioxaphosphepin 4-oxides/sulphides have exhibited good anticholinesterase activity[1,2] *in vitro*. In view of the various applications commonly associated with organophosphorus heterocycles, the previously unknown title compounds have been synthesized and their NMR (^{1}H, ^{13}C and ^{31}P) spectra have been studied.

RESULTS AND DISCUSSION

The structure and numbering of the new 2-substituted-3-(4-methylphenyl)-naphthoxazaphosphorine 2-oxides/sulphides, **1A–1K**, **2**, **3A–3D** and **4** are shown in Fig. 1 and their physical data, ^{1}H, ^{13}C and ^{31}P NMR data are presented in Tables 1–4 and 7. The synthetic procedures for typical compounds of this series are described in the Experimental section. The ^{13}C NMR data for some 4-substituted-dinaphthodioxaphosphepin 4-oxides/sulphides **5A–5H**, **6A–6E**, Fig. 2) are

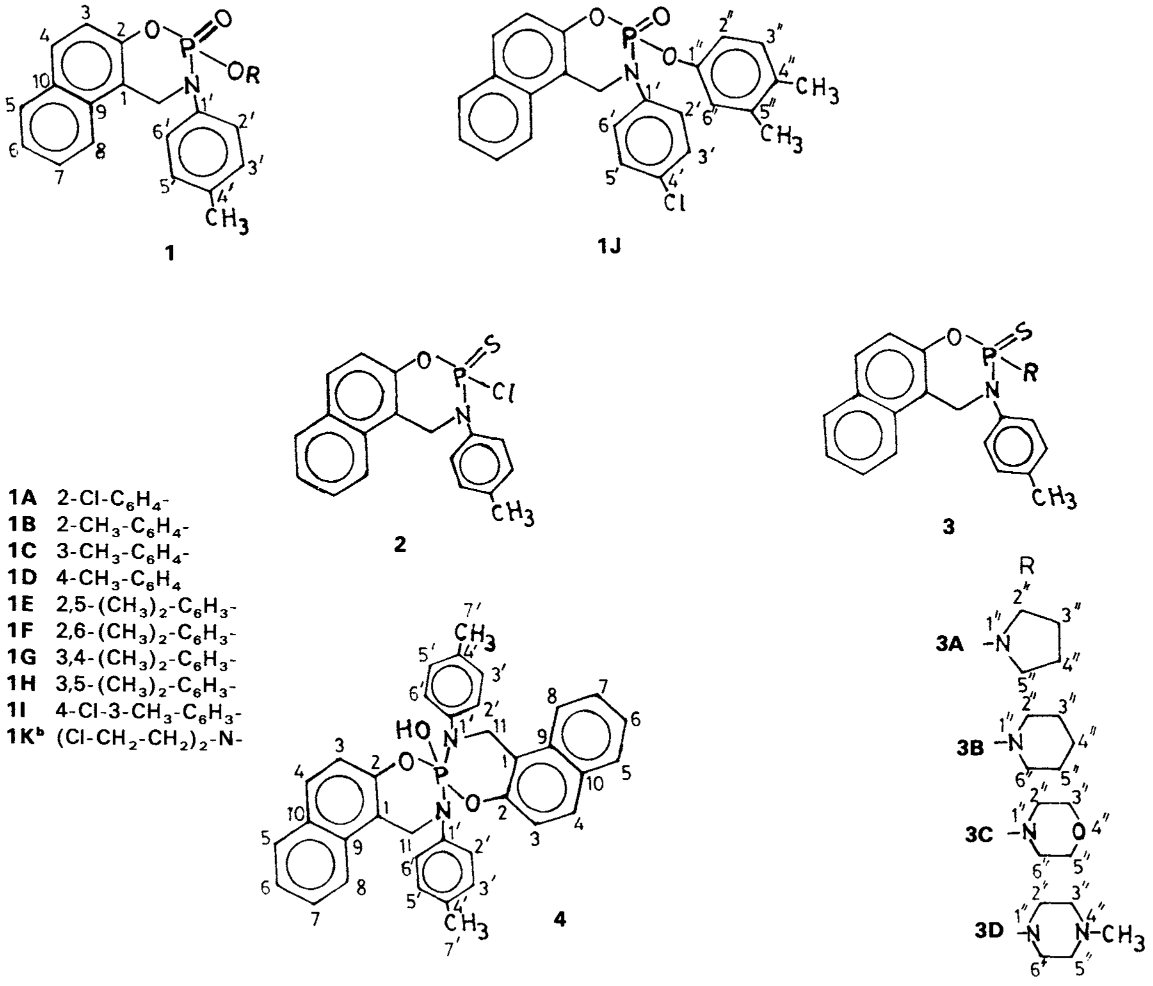

Figure 1.[a] 2-Aryloxyl/cyclicamino-2,3-dihydro-3-(4-methylphenyl)-1*H*-naphth[1,2-*e*][1,3,2]oxazaphosphorine 2-oxides/sulphides

[a] The numbering on the formulae is only for spectral comparison.

[b] Nitrogen directly attached to P-2, i.e. the oxygen (single bonded) attached to P-2 in the general formula **1** is absent.

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Table 1. Physical[a] and ^1H NMR spectral data[b] of 2-aryloxy/cyclicamino-3-(4-methyphenyl)-1*H*-naphth [1,2-*e*] [1,3,2] oxazaphosphorine 2-oxides/sulphides

Compound No.	Yield (%)	m.p. (°C)	Methyl-H	Methylene-H (m, 2H)	Ar-H	R-H
1A	70	50–52	2.20 (s, 3H)	4.50–5.25	6.70 7.55 (m, 14H)	—
1B	70	45–47	2.16 (s, 3H), 2.37 (s, 3H)	4.85–5.42	6.95–7.55 (m, 14H)	—
1C	68	110–112	2.24 (s, 3H), 2.35 (s, 3H)	4.90–5.37	6.99–7.95 (m, 14H)	—
1D	74	60–63	2.34 (s, 3H), 2.27 (s, 3H)	4.45–5.38	6.93–7.91 (m, 14H)	—
1E	58	128–130	1.93 (s, 3H), 2.20 (s, 3H) 2.32 (s, 3H)	4.88–5.32	6.75 7.87 (m, 13H)	—
1F	63	142–144	2.15 (s, 6H), 2.35 (s, 3H)	4.90–5.55	6.90–7.95 (m, 13H)	—
1G	61	143–145	2.05 (s, 6H), 2.25 (s, 3H)	4.60–5.06	6.40–7.60 (m, 13H)	—
1H	76	162–164	2.20 (s, 6H), 2.37 (s, 3H)	4.86–5.35	6.75–7.90 (m, 13H)	—
1I	66	123–124	2.35 (s, 3H), 2.40 (s, 3H)	4.90–5.37	6.80 7.95 (m, 13H)	—
1J	60	135–136	2.13 (s, 3H), 2.06 (s, 6H)	4.01–4.44	6.33–7.95 (m, 13H)	—
1K	54	98–99	—	—	—	—
2	85	158–160	2.32 (s, 3H)	4.81–5.38	6.59–7.82 (m, 10H)	—
3A	85	75–76	2.41 (s, 3H)	4.56–5.23	6.93–7.88 (m, 10H)	1.78–2.15 (m, 4H) 3.28–3.42 (m, 4H)
3B	71	157–159	2.39 (s, 3H)	4.78–5.21	7.29–7.90 (m, 10H)	1.63–3.20 (m, 10H)
3C	66	130–132	2.27 (s, 3H)	4.34–5.10	6.65–7.67 (m, 10H)	3.40–3.71 (m, 8H)
3D	63	137–139	2.27 (s, 3H)	4.50–5.41	7.05–7.82 (m, 10H)	2.55–3.30 (m, 8H) 2.35 (s, 3H, N-CH_3)
4	80	133–135	2.03 (s, 3H) 2.20 (s, 3H)	4.57–5.40 (m, 4H)	6.52–7.82 (m, 20H)	—

[a] All the compounds gave satisfactory C, H analyses.
[b] Chemical shifts (δ) in ppm from TMS.

Table 2. ^{13}C Chemical shifts[a,b] of the naphth[1,2-*e*][1,3,2] oxazaphosphorine 2-oxide/sulphide moiety

Compound No.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11 (-CH_2-)
1D	114.65 (d, J = 6.8)	147.45 (d, J = 7.9)	118.95 (d, J = 9.0)	127.34	127.34	129.91	125.17	129.91	139.33	130.26	51.23
1E	114.68 (d, J = 7.7)	148.02 (d, J = 8.5)	119.03 (d, J = 8.9)	127.41	127.41	129.96	125.57	129.96	135.93	130.29	51.29
1F	114.46 (d, J = 6.1)	147.81 (d, J = 9.1)	118.78 (d, J = 7.1)	128.67	128.67	129.78	125.00	130.06	139.30	130.06	50.29
1H	114.64 (d, J = 6.9)	148.00 (d, J = 7.7)	119.05 (d, J = 9.2)	128.75	128.90	129.92	124.85	129.92	135.82	130.82	51.25
1I	114.51 (d, J = 8.1)	147.74 (d, J = 8.1)	118.76 (d, J = 9.8)	127.90	128.77	130.01	125.30	130.01	137.52	130.27	51.29
1J	113.86	146.34 (d, J = 8.7)	119.45	128.78	128.83	131.63	122.12	131.63	—	130.60	38.97
1K	116.34 (d, J = 7.8)	144.21	119.14	128.58	129.84	129.84	126.80	130.67	—	130.25	49.89
2	113.88 (d, J = 8.6)	146.76 (d, J = 12.7)	118.46 (d, J = 9.7)	127.63	128.89	130.11	125.59	130.05	139.19	130.43	52.74
4	114.64 (d, J = 7.0)	148.18 (d, J = 11.5) 147.41 (d, J = 12.3)	119.43 118.60 (d, J = 7.9)	128.18	128.89	130.87	125.77 125.63	130.87	137.97	130.54	51.74 45.39

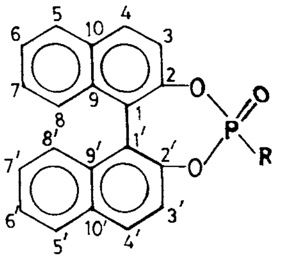
[a] Chemical shifts (δ) in ppm from TMS and J(CP) in Hz
[b] The spectra of compounds **2** and **4** were recorded on a Bruker 500 MHz spectrometer and those of the other compounds on a GE QE 300 MHz spectrometer.

Reference Data

Table 3. ^{13}C **Chemical shifts of the *N*-phenyl moiety of the naphthoxazaphosphorine 2-oxides/sulphides**

Compound No.	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′ (Ar–CH_3)
1D	139.33	124.80	128.79	129.82	128.79	124.80	20.74
1E	139.39	125.00	128.85	129.86	128.85	125.20	20.78
1F	139.32 (d, J = 5.4)[a]	125.55	128.83	129.87	128.83	125.55	20.72
1H	135.82	121.68	126.72	129.74	126.72	121.68	21.16
1I	136.08	121.60	127.43	129.85	127.43	121.60	20.82
1J	146.80	113.86	130.44	123.75	130.44	113.86	—
1K	—	126.59	128.77	130.09	128.77	126.59	20.44
2	138.17 (d, J = 2.5)[a]	121.54	127.33	129.70	127.33	121.54	21.12
4	137.09	122.46	127.76	129.77	127.56	121.90	20.93
				129.89			20.74

[a] J(CP) in Hz.



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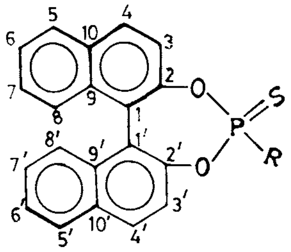

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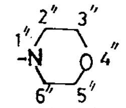
5A	3-CH_3-C_6H_4-O
5B	3,4-$(CH_3)_2$-C_6H_3-O
5C	3,5-$(CH_3)_2$-C_6H_3O
5D	2,5-$(CH_3)_2$-C_6H_3-O
5E	2,6-$(CH_3)_2$-C_6H_3-O
5F	C_6H_{11}-O
5G	Cl-CH_2-CH_2-O
5H	(Cl-CH_2-CH_2-$)_2$N-

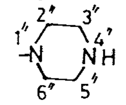
R

6A

6B



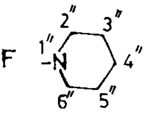
6C



6D $-\underset{H}{N}-C_6H_{11}$

6E $-N(C_4H_9)_2$

6F



6G

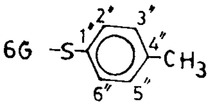


Figure 2.[a] 4-Substituted-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphephin 4-oxides/sulphides.

[a] The numbering on the formulae is only for spectral comparison.

given in Tables 5 and 6; their syntheses, IR, ^{1}H, ^{31}P NMR and mass spectral data have already been published.[3,4]

The methylene protons of the oxazaphosphorine ring moiety resonate as a multiplet of seven lines,[5] due to coupling with phosphorus, in the range of 4.01–5.55 ppm.

The interpretation of ^{13}C NMR chemical shifts was based on (1) the lower signal intensity of the non-protonated aromatic carbons (2) the coupling constants of the carbons with phosphorus and (3) calculated values. The coupling constants of 7.7–12.7 Hz ^{2}J(POC-2), 6.1–8.6 Hz ^{3}J(POCC-1) and 7.1–9.8 Hz ^{3}J(POCC-3) corroborated well with those of triaryl phosphates.[6,7] However, the methylene carbon (C-11) did not exhibit a coupling with phosphorus, ^{2}J(PNC-11). The replacement of the phenoxy group by a bis(2-chloroethyl)amino group (**1K**) caused C-1 to be deshielded by ~2 ppm whereas C-2 is shielded by about 2 ppm (*ca.* Table 2). In compound **4**, C-2, C-3, C-7 and C-11 each exhibited two signals, indicating their nonequivalence in the two oxazaphosphorine ring systems of the spiro compound. Most of the corresponding carbons of the two

Table 4. ^{13}C **NMR Chemical shifts of the 2-phenoxy and other moieties of the naphthoxazaphosphorine 2-oxides/sulphides**

Compound No.	C-1″	C-2″	C-3″	C-4″	C-5″	C-6″	-OAr-CH_3
1D	148.21 (d, J = 8.2)[a]	119.94 (d, J = 3.4)	129.99	134.60	129.99	119.94 (d, J = 3.4)	20.53
1E	148.81 (d, J = 7.5)	125.74 (d, J = 5.1)	130.82	127.41	136.90	120.16	15.37 20.78
1F	148.13 (d, J = 10.1)	129.66 (d, J = 4.7)	129.88	125.04	129.88	129.66 (d, J = 4.7)	16.96 17.01
1I	148.71 (d, J = 8.1)	122.52 (d, J = 3.8)	138.95	130.47	130.27	118.78 (d, J = 3.9)	20.20
1H	150.21 (d, J = 8.2)	117.82 (d, J = 3.6)	139.30	127.36	139.30	117.82 (d, J = 3.6)	20.88
1J	147.95	123.72 (d, J = 6.0)	138.60	134.37	—	117.89	19.67 19.06
1K	68.12 (s, 2C, C-1″), 44.47 (s, 2C, C-2″)						
3A	49.03 (d, J = 3.8, 2C, C-2″ & C-5″), 26.43 (s, 2C, C-3″ & C-4″)						

[a] Values in parentheses are for J(CP) in Hz.

Table 5. ^{13}C **Chemical shifts of the dinaphthodioxaphosphepin 4-oxide/sulphide moiety**[a,b]

Compound No.	C-1 & C-1′	C-2 & C-2′	C-3 & C-3′	C-4 & C-4′	C-5 & C-5′	C-6 & C-6′	C-7 & C-7′	C-8 & C-8′	C-9 & C-9′	C-10 & C-10′
5A	121.02	145.94 (d, J = 7.4)	120.15	131.54	129.29	127.79	126.32	126.74	132.07	131.01
	121.33	147.29 (d, J = 11.2)	120.34	131.79	129.44	—	127.00	—	—	131.18
5B	121.16	146.12 (d, J = 8.0)	120.15	132.22	128.48	126.78	126.95	125.34	131.68	131.90
	121.47	147.47 (d, J = 12.1)	120.62	—	128.39	—	127.24	—	131.52	131.65
5C	121.90	—	120.35	130.85	128.67	126.90	127.12	126.68	132.20	131.62
	120.90		120.20	130.77	—	—	127.13	126.78	132.15	131.59
5D	121.15	146.20 (d, J = 10.9)	120.59	131.53	129.39	126.80	126.94	125.84	132.15	131.53
	121.42	147.47 (d, J = 11.5)	120.57	131.08	129.44	—	127.11	—	132.19	131.60
5E	121.08	146.19 (d, J = 8.3)	120.52	131.47	128.48	127.03	126.69	125.77	132.07	131.09
	121.36	147.46 (d, J = 12.5)	120.34	131.81	128.39	—	126.77	—	—	130.95
5F	121.45	146.40	120.30	131.33	128.27	127.18	126.65	—	132.22	131.53
	121.29	147.48	120.27	131.21	128.44	—	126.97	—	132.28	131.79
5G	121.21	145.06 (d, J = 8.4)	120.33	131.44	128.37	126.73	126.94	125.77	132.03	131.76
	120.94	147.06 (d, J = 10.9)	119.93	131.47	—	126.81	—	—	—	131.55
5H	121.44	145.97 (d, J = 8.0)	120.39	130.53	128.38	125.83	127.03	126.78	132.09	131.71
	121.27	147.12 (d, J = 11.1)	120.06	130.80	128.44	—	126.90	—	—	131.42
6A	122.24	146.93 (d, J = 9.5)	121.72	130.58	128.47	126.40	127.22	125.59	132.42	131.37
	122.37	148.82 (d, J = 13.6)	120.84	130.79	128.38	126.65	126.99	125.47	—	131.82
6B	122.23	148.52	121.79	130.59	128.42	126.86	126.57	125.35	132.50	131.47
	122.15		—	130.70	128.14	—	126.23	125.10	—	131.88
6C	122.17	146.47 (d, J = 11.0)	120.24	131.38	128.28	127.15	126.97	126.18	132.20	
	122.25	147.74 (d, J = 8.5)	120.35	—	—	—	—	—	132.27	131.30
6D	121.80	148.50	120.44	131.24	128.26	126.92	127.09	126.13	132.34	131.31
	121.95	152.48	120.33	131.35	128.49	—	126.98	126.24	132.12	131.86
6E	121.13	148.84 (d, J = 14.1)	121.33	130.92	128.34	126.06	127.06	126.84	132.56	132.56
	122.31	148.63 (d, J = 8.5)	121.47	131.41	128.39	—	126.31	126.90	—	—

[a] The spectra of compounds **5A**, **5D**, **5E**, **5F** and **5H** were recorded on a Bruker 500 MHz spectrometer and those of the other compounds on a GE QE 300 MHz spectrometer.

[b] Values in parentheses are for J(CP) in Hz.

Reference Data

Table 6. ^{13}C **Chemical shifts of the 4-phenoxy and other moieties of the dinaphthodioxaphosphepin 4-oxides/sulphides**[a]

Compound No.	C-1″	C-2″	C-3″	C-4″	C-5″	C-6″	Methyl Carbons
5A	150.08 (d, J = 7.4)	119.97	140.10	126.34	129.43	116.76 (d, J = 4.0)	20.30
5B	148.28 (d, J = 6.7)	120.79 (d, J = 4.0)	138.37	133.90	130.57	116.94 (d, J = 4.7)	18.96
5C	—	117.66	139.63	127.83	139.63	117.60	20.53
5D	148.84 (d, J = 7.2)	125.73 (d, J = 6.7)	131.04	126.24	135.26	120.05 (d, J = 7.3)	15.69 20.79
5E	148.46 (d, J = 9.3)	129.09 (d, J = 5.1)	129.74	125.60	129.74	129.09 (d, J = 5.1)	17.07
5F	79.99 (d, J = 6.0)	33.43 (d, J = 4.2)	25.99	24.06	25.99	33.14 (d, J = 4.4)	—
5G	68.63 (d, J = 4.3)	42.06					
5H	68.62	42.60					
6A	48.96 (d, J = 3.5, C-2″ & C-5″), 26.43 (s, 2C, C-3″ & C-4″)						
6B	42.98 (s, 2C, C-2″ & C-6″), 63.18 (s, 2C, C-3″ & C-5″)						
6C	45.65 (s, 4C, C-2″, C-3″, C-5″ & C-6″)						
6D	50.72 (d, J = 3.8)	30.08 (d, J = 4.1)	25.40	24.28	25.13	30.532 (d, J = 3.9)	—
6E	47.68 (s, 1C, C-1″), 27.69 (s, 1C, C-2″), 18.42 (s, 1C, C-3″), 13.60 (s, 1C, C-4″)						

[a] Values in parentheses are for J(CP) in Hz.

naphtho rings in the dinaphthodioxaphosphepin 4-oxide/sulphide moieties gave two signals. There is no appreciable change in the carbon chemical shifts when the 4-oxide is replaced by a 4-sulphide group (*ca.* Table 5). The ^{13}C resonances and the coupling constants of the phenoxy moiety corroborated well with those of triaryl phosphates.[6,7,8] The ^{31}P NMR shifts in the naphthoxazaphosphorine 2-oxides (−3 to −8 ppm) and the 2-sulphide (+58 ppm) are consistent[7,9] with the structures proposed.

EXPERIMENTAL

The spectra of the title compounds were recorded in 8 mm o.d. tubes at 25 °C for $CDCl_3$ solutions with TMS as internal standard. The ^{1}H NMR spectra were recorded on a Varian EM-390 90 MHz or a Jeol FX 90 MHz spectrometer and the ^{13}C NMR spectra on GE QE-300 or Bruker 500 MHz spectrometers operating at 75.45 and 125.759 MHz, respectively. For ^{13}C, typical conditions were: sweep width 29411.8 Hz, pulse width 2.0 μsec., acquisition time 1 sec and the number of scans was 800–1500. The ^{31}P NMR spectra were recorded on a Bruker WM-250 or a Bruker WM-300 MHz spectrometer operating at 101.2 and 121.4 MHz, respectively, using 85% phosphoric acid as an external standard. All downfield shifts are positive and are on the δ scale.

Table 7. ^{31}P **Chemical shifts of the naphthoxazaphosphorine 2-oxides/sulphides**

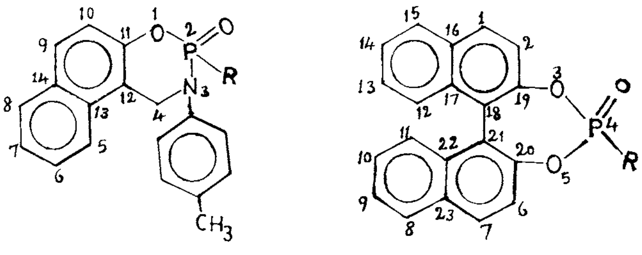
Compound No.	$\delta p^{a,b}$
1C	−2.65 −2.63
1F	−7.52
1G	−2.84 −3.01
1H	−7.64
1I	−8.44
2	+57.47 +58.79

[a] The spectra of 1C and 1G were recorded on a Bruker WM 250 MHz spectrometer and the other compounds on a Bruker WM 300 MHz spectrometer.

[b] The two signals for some compounds may be due to the existence of positional isomers (or epimers) in solution at room temperature, see D. G. Gorenstein, R. Rowell and J. Findlay, *J. Amer. Chem. Soc.* **102**, 5077 (1980).

2-(3-Methylphenoxy)-2,3-dihydro-3-(4-methylphenyl)-1*H*-naphth-[1,2-*e*][1,3,2]oxazaphosphorine 2-oxide (1C)

To a stirred and cooled (10–15 °C) solution of 1-*p*-toluidino methyl-2-naphthol (2.63 g, 0.01 mol) and anhydrous triethylamine (2.02 g, 0.02 mol) in benzene (40 ml) and tetrahydrofuran (10 ml) was added dropwise 3-methyl phenylphosphorodichloridate (2.25 g, 0.01 mol) in benzene (30 mol). After the addition, the reaction mixture was stirred at room temperature for 2 h. A solid product was obtained after filtering off the triethylamine hydrochloride and removal of the solvent in a rotavapor; **1C** (2.82 g, 68%) m.p. 110–112 °C (propan-2-ol); calculated for $C_{25}H_{22}NO_3P \cdot H_2O$, C 69.28, H 5.54; found, C 68.94, H 5.81%. IR (Nujol): 1620, 1610, 1535, 1515, 1460, 1380, 1350, 1300 (P = 0), 1220 (P–O–C_{ar}), 1160, 1140, 1080 (P–N–C_{ali}), 1000, 960 (P–O–C_{ar}), 900, 875, 820, 780 and 710 cm^{-1}. MS, *m*/*z* (relative intensity): 415 (89.3, $M^{+\cdot}$) 324 (15.3), 309 (22.5), 308 (100.0),



1 **5**

Figure 3. Nomenclature of compounds **1** and **5**. Compound **1**. 2-Substituted-2,3-dihydro-3-(4-methylphenyl)-1*H*-naphth[1,2-*e*][1,3,2] oxazaphosphorine 2-oxide. Compound **5**. 4-Substituted-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2] dioxaphosphepin 4-oxide.

Reference Data

261 (24.8), 246 (14.7), 245 (74.8), 149 (41.0), 91 (18.6).

2-Chloro-2,3-dihydro-3-(4-methylphenyl)-1*H*-naphth[1,2-*e*][1,3,2]oxazaphosphorine 2-sulphide

(2)

A solution of thiophosphoryl chloride (1.7 g, 0.01 mol) in benzene (20 ml) was added to a stirred and cooled (10–15 °C) solution of 1-*p*-toluidinomethyl-2-naphthol (2.63 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in benzene (40 ml) and tetrahydrofuran (10 ml). The reaction mixture was stirred at room temperature for 2 h and later at 45–65 °C for another 2 h. The usual work up gave **2** (3.0 g, 85%), m.p. 158–160 °C (propan-2-ol); calculated for $C_{18}H_{15}NOPSCl$; C 60.16, H 4.17; found, C 60.37, H 4.50. IR (KBr): 2950, 2920, 1625, 1605, 1510, 1465, 1450, 1430, 1400, 1330, 1625 (P = 0), 1220 ($P–O–C_{ar}$), 1180, 1115, 1105, 1065 ($P–N–C_{ali}$), 1020, 995 970 ($P–O–C_{ar}$), 900, 860, 820, 785 and 750 (P = S) cm^{-1}. MS, *m/z* (relative intensity): 361 (22.2, M + 2), 360 (14.3, M + 1), 359 (63.4, $M^{+\cdot}$), 328 (36.0), 327 (21.3), 326 (100), 245 (20.9), 157 (15.0), 115 (22.0), 114 (15.0), 107 (68.0), 106 (33), 77 (82.0).

2-(1-Pyrrolidinyl)-2,3-dihydro-3-(4-methylphenyl-1*H*-naphth[1,2-*e*][1,3,2]oxazaphosphorine2-sulphide

(3A)

A solution of thiophosphoryl chloride (1.7 g, 0.01 mol) in benzene (20 ml) was added to a stirred solution of 1-*p*-toluidinomethyl-2-naphthol (2.63 g, 0.01 mol) and triethylamine (3.03 g, 0.03 mol) in benzene (40 ml) and tetrahydrofuran (10 ml) at 10–15 °C. The reaction mixture was stirred at room temperature for 2 h, and later at 45–65 °C for another 2 h and cooled to 10–15 °C. A solution of pyrrolidine (0.71 g, 0.01 mol) was added dropwise and the mixture was stirred at room temperature for 2 H. The usual work up gave **3A** (3.3 g, 85%), m.p. 75–76 °C (propan-2-ol); calculated for $C_{22}H_{23}O_2PS$; C 67.00, H 5.83; found, C 67.25, H 6.10. (IR (KBr): 2950, 2920, 1625, 1600, 1520, 1465, 1430, 1400, 1330, 1215 ($P–O–C_{ar}$), 1180, 1115, 1105, 1065 ($P–N–C_{ali}$), 980 ($P–O–C_{ar}$), 885, 815, 780 and 750 (P = S) cm^{-1}. MS, *m/z* (relative intensity): 394 (3.4, $M^{+\cdot}$), 362 (6.4), 361 (30.0), 360 (12.2), 359 (70.3), 358 (4.4), 329 (10.0), 328 (40.0), 327 (28.0), 326 (100), 292 (11.0), 246 (8.0), 245 (28.0), 244 (29.5), 203 (10.0), 168 (70.0), 136 (40.0), 128 (20.0), 115 (12.0), 90 (29.0), 70 (25.0.

2-Hydroxy-2,2′-spirobi[2,3-dihydro-3-(4-methylphenyl)-1*H*-naphth[1,2-*e*][1,3,2]oxazaphosphorine]

(4)

Phosphorus oxychloride (1.53 g, 0.01 mol) in benzene (20 ml) was added to a cooled (5–10 °C) and stirred solution of 1-*p*-toluidino methyl-2-naphthol (2.63 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in benzene (40 ml) and tetrahydrofuran (10 ml). After the addition, the reaction mixture was stirred at room temperature for 2 h and another 2 h at 45–60 °C. The crude product obtained after removing triethylamine hydrochloride and the solvent was run through a chromatographic column of silica gel and eluted with a mixture of benzene-ethyl acetate (3:1) to afford **4** (4.5 g, 80%), m.p. 133–135 °C; calculated for $C_{36}H_{31}N_2O_3P$; C 75.78, H 5.43; found C 76.10, H 5.66. IR (KBr): 1620, 1590, 1505, 1460, 1430, 1330, 1295, 1260, 1215 ($P–O–C_{ar}$), 1065 ($P–N–C_{ali}$), 1020, 980, 915, 810, 750 and 535 cm^{-1}. MS, *m/z* (relative intensity): 571 (1.8 M + 1), 570 (4.3, $M^{+\cdot}$), 466 (1.2), 465 (3.9), 464 (3.9), 463 (6.9), 414 (1.4), 399 (1.2), 326 (1.7), 325 (7.2), 324 (2.4), 309 (1.7), 308 (7.5), 307 (66.0), 253 (1.2), 245 (89.5), 106 (100).

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