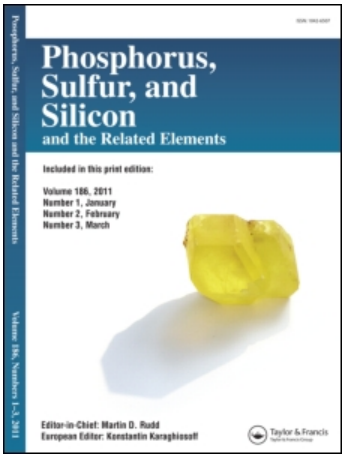

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS, ^{1}H, ^{13}C, ^{31}P NMR ANALYSIS, AND INSECTICIDAL ACTIVITY OF MEMBERS CONTAINING EXTERNAL P—O OR P—N BONDS IN 6-SUBSTITUTED-2,10-DICHLORO-12*H*-DIBENZO[*d,g*][1,3,2]DIOXAPHOSPHOCIN 6-OXIDES

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To cite this Article Reddy, C. Devendranath , Berlin, K. Darrell , Reddy, R. Suryanarayana , Raju, C. Naga , Elmasri, Marwan and Subramanian, Shankar(1993) 'SYNTHESIS, ^{1}H, ^{13}C, ^{31}P NMR ANALYSIS, AND INSECTICIDAL ACTIVITY OF MEMBERS CONTAINING EXTERNAL P—O OR P—N BONDS IN 6-SUBSTITUTED-2,10-DICHLORO-12*H*-DIBENZO[*d,g*][1,3,2]DIOXAPHOSPHOCIN 6-OXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 81: 1, 61 — 71
To link to this Article: DOI: 10.1080/10426509308034374
URL: http://dx.doi.org/10.1080/10426509308034374

Phosphorus, Sulfur, and Silicon, 1993, Vol. 81, pp. 61–71
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SYNTHESIS, ^{1}H, ^{13}C, ^{31}P NMR ANALYSIS, AND INSECTICIDAL ACTIVITY OF MEMBERS CONTAINING EXTERNAL P—O OR P—N BONDS IN 6-SUBSTITUTED-2,10-DICHLORO-12*H*-DIBENZO[*d*,*g*][1,3,2]DIOXAPHOSPHOCIN 6-OXIDES

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(Received April 8, 1993; in final form May 4, 1993)

The synthesis of novel 6-substituted-2,10-dichloro-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-oxides is described along with IR, ^{1}H, ^{13}C, and ^{31}P NMR spectral data. Phosphorus couplings of $^{5}J_{PH}$, $^{2}J_{POC}$ and $^{3}J_{POCC}$ were determined. An appraisal of the data in total did not allow unequivocal differentiation between a boat-boat, boat-chair, distorted boat, or twist boat conformation for the eight-membered ring of the dioxaphosphocin 6-oxides. A few members of this family were evaluated for toxicity in the insect *P. americana*.

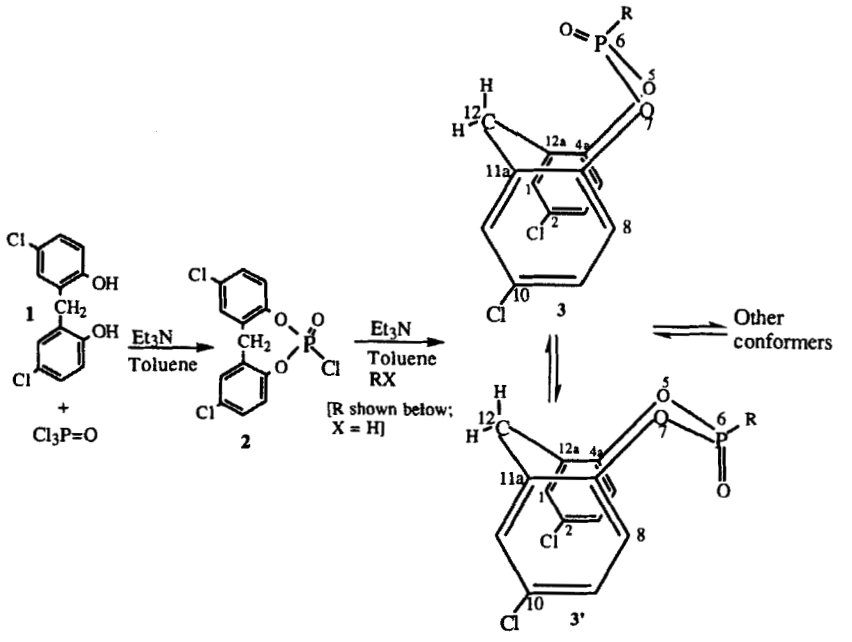
Key words: 6-Substituted-2,10-dichloro-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-oxides; NMR analysis; conformational analysis; toxicity in insects.

INTRODUCTION

Several organophosphorus pesticides are valuable[1] and have been part of a continued study from our groups.[2–4] We report the syntheses and conformational analyses of 6-substituted-2,10-dichloro-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-oxides containing external P(6)—O and P(6)—N bonds. Confirmation of structures was achieved via evaluation of IR, ^{1}H, ^{13}C, and ^{31}P spectral data on solutions. Preliminary toxicity of a few members was assessed in certain insects.

RESULTS AND DISCUSSION

A condensation of 5,5′-dichloro-2,2′-dihydroxydiphenylmethane (**1**) with phosphorus oxychloride in toluene/triethylamine at 40–50°C produced slightly crude acid chloride **2**. TLC analysis indicated the conversion to **2** was complete within three hours. To the same vessel (0–5°C) containing crude **2** was added a solution of a cyclic amine or an alcohol in toluene/triethylamine. Critical points in the procedure involved stirring the resulting mixture at room temperature (1 hour) followed by additional stirring at 40°C (2 hours). Filtration of the triethylamine hydrochloride, followed by evaporation of the solvent, gave the solid title com-



pounds all of which could be recrystallized from ethanol. Spectral data, physical properties, and elemental analyses of the products are recorded in Tables I–VII. Characteristic IR frequencies were observed for $\nu_{P=O}$,[5] $\nu_{P-O-C(arom)}$,[6,7] $\nu_{P-N-C(aliph)}$,[8] and $\nu_{P-O-C(aliph)}$[6] groups (Table I).[9]

In the ^{1}H NMR spectra, the aromatic protons gave three separate signals for three sets of protons in **3a–3h** from the dioxaphosphocin moiety. A doublet of doublets in the region δ 7.00–7.05 (J = 8.6 and 1.5 Hz) was assigned to H(4) and H(8). Another doublet of doublets at δ 7.15–7.18 (J = 8.6 and 2.3 Hz) was attributed to H(3) and H(9). Both H(1) and H(11) resonated as a doublet (J = 1.4 Hz) at δ 7.26–7.45 (Table II). In the compounds **3i–3q**, the protons from CH_2 and CH_3 groups appeared in normal ranges while the aromatic protons of the

TABLE I

Physical data[a] and IR absorptions of **3a–3q**

Compd.	Yield (%)	MP (°C)	MF	IR(cm^{-1}) $\upsilon_{P=O}$	$\upsilon_{P-O-C(arom)}$		$\upsilon_{P-N-C(aliph)}$ $\upsilon_{P-O-C(aliph)}$	
3a	38[b]	209-10	$C_{17}H_{16}O_3Cl_2NP$	1280	1240	930	740	1015
3b	30[b]	239-41	$C_{18}H_{18}O_3Cl_2NP$	1260	1240	930	760	1040
3c	28[b]	214-15	$C_{17}H_{16}O_4Cl_2NP$	1270	1230	930	740	980
3d	26[b]	255-56	$C_{17}H_{16}O_3Cl_2NSP$	1270	1235	925	740	1020
3e	25[c]	260-61	$C_{18}H_{19}O_3Cl_2N_2P$	1270	1235	930	735	980
3f	25[c]	160-61	$C_{16}H_{14}O_3Cl_2NSP$	1270	1230	930	740	990
3g	40[c]	110-11	$C_{17}H_{18}O_3Cl_2NP$	1285	1235	925	735	1040
3h	36[c]	96-97	$C_{21}H_{26}O_3Cl_2NP$	1280	1230	930	740	1040
3i	42[c]	105-06	$C_{14}H_{11}O_4Cl_2P$	1290	1230	940		1175
3j	40[c]	162-63	$C_{15}H_{13}O_4Cl_2P$	1295	1240	935		1170
3k	36[c]	140-41	$C_{16}H_{15}O_4Cl_2P$	1290	1235	940		1180
3l	45[b]	136-37	$C_{16}H_{15}O_4Cl_2P$	1280	1240	935		1170
3m	39[c]	185-86	$C_{17}H_{17}O_4Cl_2P$	1275	1230	940		1168
3n	36[b]	168-69	$C_{17}H_{17}O_4Cl_2P$	1285	1235	935		1180
3o	28[c]	146-47	$C_{18}H_{19}O_4Cl_2P$	1295	1235	940		1170
3p	39[b]	138-39	$C_{19}H_{19}O_4Cl_2P$	1290	1240	940		1170
3q	40[c]	158-60	$C_{20}H_{15}O_4Cl_2P$	1290	1235	940		1170

[a]All the compounds gave satisfactory C and H analysis.
[b]Recrystallized from ethanol.
[c]Recrystallized from methanol-benzene.

TABLE II

^{1}H NMR data of dioxaphosphocin and cyclic (**3a–ef**) and acylic (**3g,3h**) amino moieties of **3a–3h**; δ values (J in Hz)

Compd.	CH_2 [H(12)] (dd, 2 H)	H(1/11)	H(3/9)	H(4/8)	R-H
3a	3.73 (13.7) 4.24 (2.5, 13.6)	7.27 (2.4)	7.16 (2.2, 8.5)	7.02 (1.6, 8.6)	1.88-2.20 (m, 4 H, 3' & 4' CH_2) 3.38-3.52 (m, 4 H, 2' & 5' CH_2)
3b	3.74 (13.4) 4.22 (2.3, 13.5)	7.26 (2.3)	7.16 (2.2, 8.6)	7.03 (1.6, 8.7)	1.53 (t, 2 H, 4'-CH_2-) 1.63-1.80 (m, 4 H, 3' & 5' CH_2) 3.33-3.36 (m, 4 H, 2' & 6' CH_2)
3c	3.80 (13.6) 4.22 (2.6, 13.6)	7.27 (2.5)	7.17 (2.2, 8.6)	7.02 (1.6, 8.7)	3.50-3.62 (m, 4 H, 2' & 6' CH_2) 3.78-3.81 (m, 4 H, 3' & 5' CH_2)
3d	3.70 (13.3) 4.22 (2.6, 13.5)	7.26 (2.5)	7.17 (2.3, 8.6)	7.02 (1.6, 8.7)	2.60-2.75 (m, 4 H, 3' & 5' CH_2) 3.67-3.76 (m, 4 H, 2' & 6' CH_2)
3e	3.73 (13.6) 4.19 (2.5, 13.5)	7.28 (2.5)	7.18 (2.4, 8.6)	7.05 (1.4, 8.6)	2.36 (s, 3 H, -N-CH_3) 2.51-2.54 (m, 4 H, 3' & 5' CH_2) 3.41-3.44 (m, 4 H, 2' & 6' CH_2)
3f	3.70 (13.6) 4.20 (2.5, 13.6)	7.28 (2.5)	7.18 (2.4, 8.6)	7.04 (1.6, 8.6)	3.09-3.14 (t, 2 H, 3' CH_2) 3.75-3.82 (m, 2 H, 5' CH_2) 4.54-4.58 (d, 2 H, 2' CH_2')
3g	3.78 (13.6) 4.17 (2.3, 13.6)	7.45 (2.5)	7.18 (2.4, 8.6)	7.04 (1.5, 8.6)	1.24-1.61 (t, 6 H, 3' CH_2) 3.26-3.39 (m, 4 H, 2' CH_2)
3h	3.80 (13.4) 4.18 (13.6)	7.26 (2.5)	7.15 (2.4, 8.6)	7.0 (1.4, 8.7)	0.96-1.10 (t, 6 H, 5' CH_3) 1.4-1.8 (m, 8 H, 3' & 4' CH_2) 3.2-3.4 (m, 4 H, 2' CH_2)

dioxaphosphocin group gave complex multiplets in the region δ 6.90–7.35 which included all six protons (Table III). In P-amides **3a–3h** the bridged methylene protons [H(12)] appeared as one doublet and one doublet of doublets in the regions δ 3.70–3.80 (d, J = 13.6 Hz) and δ 4.17–4.24 (dd, J = 13.6 and 2.5 Hz). The reason for the downfield doublet being split into a doublet is due to long range coupling ($^5J_{H\text{-}P}$)[10–12] between phosphorus and one of the methylene protons to the extent of ~2.5 Hz. The coupling constant J = 13.6 Hz was attributed to geminal coupling between the two bridged methylene protons ($^2J_{H\text{-}H}$). In P-esters **3i–3q** signals for the bridged methylene protons merged with proton resonances from the alkoxy moieties. Thus the coupling constants of bridged methylene protons could not be determined (Table III) in these cases.

Controvery exists regarding preference for a boat-chair (BC), a boat-boat (BB), a twist-boat (TB) or a distorted boat (DB) conformation for the dibenzodioxaphosphocin ring system in solution.[4] At 253 K, for example, 6-ethoxy-2,4,8,10-tetramethyl-*endo*-12*H*-isopropyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-oxide (R = isopropyl) was suggested to have a high population in $DCCl_3$ of a boat-boat (shown top of page 6) or possibly a twist-boat form.[4d] Certain X-ray diffraction data on solid members of the dioxaphosphocins have suggested the boat-chair form as preferred in some cases except where large groups are at the 4- and 8-positions

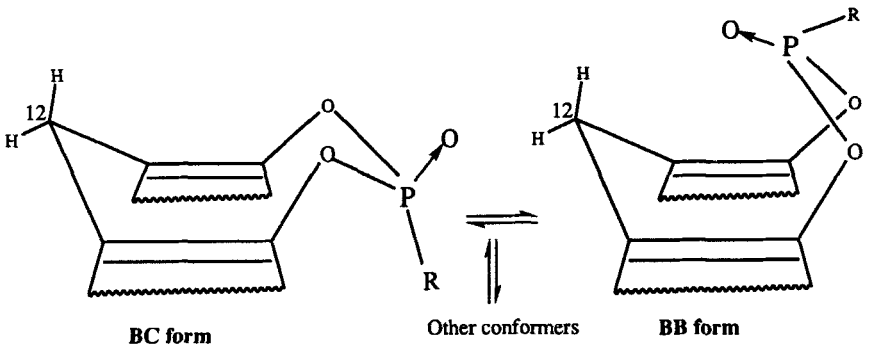
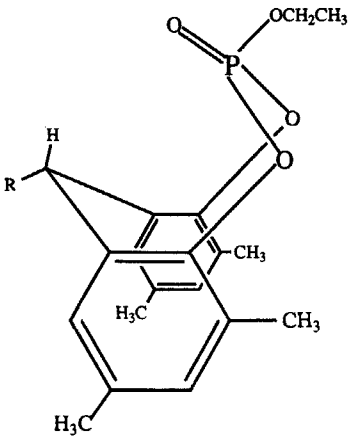


TABLE III

^{1}H NMR data of dioxaphosphocin and alkoxy moieties of **3i–3q**; δ values

Compd.	CH_2 [H(12)] (dd, 2 H)	Ar-H (m, 6 H)	R-H
3i	3.60-4.22	6.99-7.32	3.90-4.12 (m, 3 H, CH_3)
3j	3.71-4.24	7.01-7.29	1.40-1.69 (t, 3 H, CH_3) 4.30-4.61 (m, 2 H, CH_2)
3k	3.70-4.30	7.01-7.31	0.95-1.15 (t, 3 H, CH_3) 1.70-1.95 (m, 2 H, CH_2) 4.20-4.1 (m, 2 H, CH_2)
3l	3.66-4.32	7.00-7.32	1.41-1.56 (d, 6 H, CH_3) 4.80-5.20 (m, 1 H, CH)
3m	3.74-4.22	7.04-7.29	0.95-1.0 (t, 3 H, CH_3) 1.44-1.56 (m, 2 H, CH_2) 1.77-1.82 (m, 2 H, CH_2) 4.33-4.41 (m, 2 H, CH_2)
3n	3.70-4.32	6.98-7.30	0.80-1.1 (d, 6 H, CH_3) 1.40-1.60 (m, 1 H, CH) 4.32-4.89 (m, 2 H, CH_2)
3o	3.75-4.22	7.03-7.29	0.85-0.95 (t, 3 H, CH_3) 1.40-1.90 (m, 6 H, CH_2) 4.32-4.39 (m, 2 H, CH_2)
3p	3.74-4.23	7.04-7.32	1.10-2.10 (m, 10 H) 4.60-4.80 (m, 1 H, -CH-)
3q	3.70-4.32	6.90-7.35 (m, 11 H)	5.51-5.50 (d, 2 H, O-CH_2)

which induce formation of a distorted boat form.[4e] The question of one preferred conformer in solution remains difficult to ascertain from NMR spectral analysis alone, but it seems certain that an equilibrium exists involving several forms in many cases.[4] These systems are reminiscent of butterfly type phosphorus-containing molecules.[13] The latter vary in ring "fluttering" with temperature and this may contribute to the variation in conformations. We had previously contended that the boat-boat form was favored, based upon spectral analysis in a related system,[4a]



but the steric effects may well be so subtle to preclude a definitive conclusion about the preferred conformation for this family of heterocycles in solution. Both the size of R in the above formula and even the size of the external group attached directly to phosphorus can influence the population of the main conformation present in solution. Moreover, both $^2J_{HH}$ and $^5J_{HP}$ couplings can be close in value for boat-chair and distorted boat forms.[4e] Unfortunately, suitable crystals could not be grown for any member in the present study to allow a single X-ray diffraction analysis of the solid state.

TABLE IV

^{13}C NMR data of dioxaphosphocin 6-oxide moiety of **3a–3q** (ppm values)

Compd.	C(1/11)	C(2/10)	C(3/9)	C(4/8)[a]	C(4a/7a)[a]	C(11a/12a)[a]	C(12) [CH_2]
3a	129.9	130.9	128.6	123.7 (4.7)	147.4 (8.5)	133.3 (3.4)	33.4
3b	129.9	130.9	128.6	123.7 (4.0)	147.6	133.3	33.5
3c	130.0	131.2	128.7	123.6 (4.0)	147.1	133.2	33.3
3d	129.9	131.2	128.7	123.7 (4.3)	147.2	133.1 (3.2)	33.4
3e	130.0	131.1	128.8	123.8 (4.9)	147.1 (8.6)	133.2 (3.5)	33.4
3f	130.1	131.3	128.8	123.6 (4.8)	147.0 (8.6)	133.1 (3.5)	33.4
3h	129.9	130.7	128.6	123.6 (4.8)	147.6 (8.6)	133.2 (3.5)	33.5
3i	130.1	131.5	128.8	123.4 (3.1)	146.6 (7.9)	133.0 (3.6)	32.8
3j	130.0	131.4	128.8	123.4	146.6 (7.7)	133.1 (3.7)	32.8
3k	130.1	131.6	129.0	123.5 (4.9)	147.9 (6.8)	133.1 (3.4)	33.0
3l	130.9	132.2	129.6	124.4 (4.8)	147.6 (7.8)	134.0 (3.7)	33.8
3m	130.1	131.5	128.9	123.6 (4.8)	146.8 (7.7)	133.2 (3.7)	33.0
3n	130.0	131.4	128.8	123.5 (4.4)	146.7 (7.8)	133.1 (3.2)	32.9
3p	130.1	131.4	128.8	123.7 (4.7)	146.9 (7.8)	133.2 (3.5)	33.2
3q	130.1	131.5	128.8	123.5 (4.8)	146.8 (8.0)	133.0 (3.6)	33.0

[a] Data in parentheses are coupling constants J_{PC} (Hz).

The influence on the conformation by the P—N bond is not well known, although the example with R = $P(S)NEt_2$ is reported to be a boat-chair.[14] It was surprising that nearly all chemical shifts for $H(12)_{ax}$ or $H(12)_{eq}$ are more downfield for members of **3a–3h** with an external P—N bond than for **3i–3q** with an external P—O bond. Conceptually the trigonal nitrogen might cause small distortions in the 8-membered ring which may flatten the system with the result of increased shifts for H(12) arising from possible increased s character in C(12).

The ^1H NMR chemical shifts of acyclic amino and heterocyclic moieties are incorporated in Table II. The data were interpreted as illustrated based upon proton chemical shifts of free amines and heterocyclic bases.[15] A deshielding influence of the dioxaphosphocin 6-oxide ring system on these protons gradually decreased with increasing distance. For example, the 2′-methylene protons (α) experienced a downfield shift to the extent of 0.6–0.9 ppm and the 3′-methylene protons (β) were 0.2–0.4 ppm whereas the 4′-methylene protons did not exhibit any significant shift.

The proton chemical shifts from the alkoxy moieties are given in Table III. The signals of these proton-containing groups were located in a downfield region when

TABLE V

^{13}C NMR data (ppm) of cyclic amino acid and alkoxy moieties of **3a–3q**

Compd	Chemical Shifts[a]
3a	26.43 [d, J = 10.3, 2 C, C(3',4')], 47.2 [d, J = 4.7, 2 C, C(2',5')]
3b	24.3 [s, C(4')], 25.7 [d, J = 3.8, 2 C, C(3',5')], 45.67 [s, 2 C, C(2',6')]
3c	44.7 [s, 2 C, C(2',6')], 66.7 [d, J = 5.9, 2 C, C(3',5')]
3d	27.0 [d, J = 3.5, 2 C, C(3',5')], 46.7 [s, 2 C, C(2',6')]
3e	44.3 [s, 2 C, C(2',6')], 46.1 [s, 1 C, -N-CH_3], 54.7 [d, J = 4.9, 2 C, C(3',5')]
3f	32.1 [d, J = 5.8, 1 C, C(4')], 50.1 [d, J = 3.0, 1 C, C(5')], 50.7 [d, J = 4.8, 1 C, C(2')]
3h	13.9 [2 C, C(4')], 19.9 [2 C, C(3')], 30.5 [2 C, C(2')], 45.7 [d, J = 3.8, 2 C, C(1')]
3i	55.6 [d, J = 6.2, C(1')]
3j	16.0 [d, J = 6.6, 1 C, C(2')], 65.9 [d, J = 6.1, 1 C, C(1')]
3k	8.5 [1 C, C(3')], 24.0 [1 C, C(2')], 68.7 [d, J = 6.1, 1 C, C(1')]
3l	24.4 [d, J = 5.0, 2 C, C(2')], 76.5 [d, J = 6.1, 1 C, C(1')]
3m	13.5 [C, C(4')], 18.6 [1 C, C(3')], 32.1 [d, J = 6.8, 1 C, C(2')], 69.6 [d, J = 6.5, 1 C, C(1')]
3n	18.5 [2 C, C(3')], 29.0 [d, J = 7.2, 1 C, C(2')], 75.5 [d, J = 6.7, 1 C, C(1')]
3p	23.4 [2 C, C(3',5')], 24.9 [1 C, C(4')], 33.2 [d, J = 4.7, 2 C, C(2',6')], 80.3 [d, J = 6.5, 1 C, C(1')]
3q	71.0 [d, J = 5.5, 1 C, C'H_2)]

[a]Chemical shifts (ppm from TMS) and J_{PC} values (Hz).

compared to the corresponding free alcohol proton resonances. It is of interest to note that the coupling with phosphorus was limited to protons on α-carbons only.

The ^{13}C NMR chemical shifts of the dibenzodioxaphosphocin 6-oxide group are given in Table IV. The oxygen-bearing carbons C(4a) and C(7a) resonated in the

TABLE VI

^{31}P NMR chemical shifts (ppm from 85% H_3PO_4) of **3a–3q**

Compd	δP	Compd	δP
3a	-1.07	**3j**	-12.03
3b	-0.76	**3k**	-11.88
3c	-1.74	**3l**	-12.81
3d	-1.55	**3m**	-11.92
3e	-1.31	**3n**	-11.94
3f	-2.74	**3o**	-11.92
3g	+0.98	**3p**	-12.84
3h	+0.72	**3q**	-11.81
3i	-10.95		

TABLE VII

C and H analyses of compounds **3a–3q**

Compd.	C Found (Calcd)	H Found (Calcd)
3a	53.10 (53.13)	4.10 (4.17)
3b	54.20 (54.27)	4.40 (4.52)
3c	50.95 (51.00)	3.90 (4.00)
3d	48.96 (49.03)	3.74 (3.85)
3e	52.24 (52.30)	4.52 (4.60)
3f	47.68 (47.76)	3.39 (3.48)
3g	52.75 (52.85)	4.53 (4.66)
3h	56.90 (57.01)	5.81 (5.88)
3i	48.76 (48.70)	3.26 (3.19)
3j	50.18 (50.14)	3.69 (3.62)
3k	51.56 (51.47)	4.12 (4.02)
3l	51.58 (51.47)	4.14 (4.02)
3m	52.79 (52.71)	4.46 (4.39)
3n	52.80 (52.71)	4.43 (4.39)
3o	53.95 (53.87)	4.81 (4.74)
3p	55.29 (55.21)	4.65 (4.60)
3q	57.06 (57.01)	3.64 (3.56)

region 146.6–147.9 ppm as a doublet, $^2J_{POC(4a)}$ and C(7a) = 8.0 Hz.[16] A doublet around 123.6 ppm ($^3J_{POC}$ = 4.5 Hz) was ascribed to C(4) and C(8).[17] A low intensity doublet in the region 133.0–134.0 ppm [$^3J_{POC—C(11a)}$ and $^3J_{POC—C(12a)}$ = 3.5 Hz] was attributed to C(11a) and C(12a). The chlorine-substituted carbons C(2) and C(10) gave signals in the region 130.7–132.2 ppm. Chemical shifts at 130.0 ppm were assigned to C(1) and C(11) while the signal at 128.8 ppm was suggested for C(3) and C(9). The bridged carbon C(12) resonated in the region 32.8–33.8 ppm.[18]

The carbon chemical shifts of the heterocyclic groups present in compounds **3a–3f** were assigned on the basis of literature data for similar atoms in the free heterocyclic bases[19–21] as well as coupling to phosphorus (Table V). The data demonstrated that carbons in the heterocyclic moiety of the dioxaphosphocin 6-oxides are shielded to the extent of 1–2 ppm relative to the corresponding values in the free bases with the exception of appropriate signals found for the pyrrolidine moiety (Table V) in **3a**. It is to be noted that C(3′) and C(4′) (β-carbons) exhibited larger coupling constants compared to C(2′) and C(6′) (α-carbons). Intuitively, this might suggest a chair-like conformation for these heterocyclic groups.[22] The di-*n*-butylamino group in **3h** gave ^{13}C signals in the expected range.

The C(1′) chemical shifts of the alkoxy functions occurred downfield (6–10 ppm) in **3i–3q** when compared to signals in the corresponding free alcohols (neat). The C(1′) carbon is coupled with phosphorus to about the same extent [$^2J_{POC(1')}$ = 5.5–6.7 Hz] as is C(2′) [$^3J_{POC(1')—C(2')}$ = 4.7–7.2 Hz]. Resonance signals for C(2′), C(3′) and C(4′) were located slightly upfield (Table V) from those found in the corresponding free alcohols.

Members **3a–3e** displayed ^{31}P signals in the range of −0.76 to −1.74 ppm while **3f** resonanted more upfield at −2.74 ppm. The other two acyclic amino derivatives (**3g** and **3h**) gave signals at +0.98 and +0.72 ppm, respectively. The 6-alkoxy derivatives **3i–3q** had signals in the region of −10.95 to −12.84 ppm (Table VI) which agreed well with the reported values[23] for somewhat related systems.

TOXICITY EVALUATION

Different concentrations of selected test compounds **3k**, **3m** and **3o** were prepared in tetrahydrofuran, and the solutions were sprayed onto the cuticle surface of the insect (*P. americana*) by a micro syringe. The mortality was noted after 24 hours. The observed data was subjected to the Finney's[24] statistical treatment to derive certain graphs, namely: (1) log concentration versus percent kill and (2) log concentration versus probit kill. As representative cases, the LD_{50} values of the test compounds **3k**, **3m** and **3o** were to be 36.2, 35.5 and 35.0 mg/kg (data taken from the above cited graphs), respectively.

EXPERIMENTAL

Microanalyses were performed at Central Drug Research Institute, Lucknow, India. IR spectra were recorded as KBr pellets on a Perkin Elmer Model 137 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz spectrometer on near saturated $DCCl_3$ solutions with the chemical shifts (referenced to TMS) reported in δ values or in ppm. The ^{13}C spectra (Table IV) of **3g** and **3o** have not been included, but will be reported elsewhere in connection with other work. All ^{31}P

NMR-spectra were recorded on $DCCl_3$ solutions using a Varian VXRD 300 spectrometer at 121 MHz with shifts (referenced to 85% H_3PO_4) reported in ppm, negative values being upfield of the standard and positive values being downfield.

2,10-Dichloro-6-(1-piperidinyl)-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-oxide (**3b**). The following procedure illustrates the general method used to prepare all the members of **3a–3q**. A solution of 2.69 g (0.01 mol) of 5,5′-dichloro-2,2′-dihydroxydiphenylmethane (**1**) in 30 ml of dry toluene was added dropwise to a cooled (0–5°C) and stirred solution containing 1.53 g (0.01 mol) of phosphorus oxychloride and 2.02 g (0.02 mol) of triethylamine in 60 ml of toluene. After stirring for 3 hours at 40–50°C, TLC analysis of the mixture on silica gel indicated the formation of the monochloride **2**. This reaction mixture was cooled to 0–5°C, and a solution of 0.85 g (0.01 mol) of piperidine and 1.01 g (0.01 mol) of triethylamine in 30 ml of toluene was added dropwise. The new reaction mixture was stirred at room temperature for 1 hour and then at 40°C for 2 hours. Filtration of triethylamine hydrochloride and evaporation of the solvent produced a residue. The solid was washed quickly with water and recrystallized from ethanol to yield 1.19 g (30%) of **3b** as a white powder, mp 239–241°C. Data for the other members are in the Tables.

$C_{18}H_{18}NO_3Cl_2P$ (397.9): Calcd: C, 54.27; H, 4.52
Found: C, 54.20; H, 4.40

MS m/z (rel. intensity): 399 (17.5, M + 2), 397 (17.5, M^+), 356 (2.5), 342 (3.9), 316 (2.3), 313 (5.2), 296 (5.2), 279 (8.0), 277 (5.2), 251 (10.6), 249 (19.0), 233 (9.2) 215 (12.2), 186 (11), 173 (6.2), 168 (4.5), 163 (3.8), 152 (11), 139 (9.6), 86 (22.6), 85 (75), 84 (100), 77 (5.9).

ACKNOWLEDGMENTS

The authors thank Hindustan Lever Research Foundation, Bombay, for financial assistance and Dr. G. V. Subba Raju for helpful discussions. One (KDB) of us gratefully acknowledges partial support for the XL-300 upgrade by the National Science Foundation (grant DMB-8603864) and OCAST (MOST program) for partial support as well (grant 1506).

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