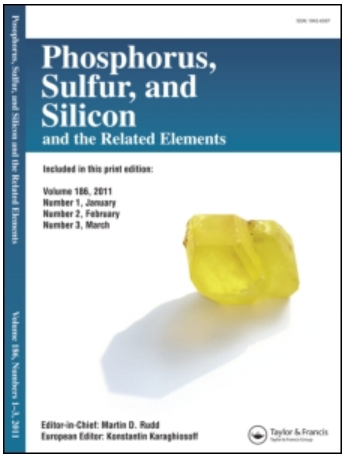

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SYNTHESIS OF 2-ARYLOXY-6-METHYL-4-TRICHLOROMETHYL-4H-1,3,2-BENZODIOXAPHOSPHORIN 2-OXIDES/SULFIDES

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SYNTHESIS OF 2-ARYLOXY-6-METHYL-4-TRICHLOROMETHYL-4H-1,3,2-BENZODIOXAPHOSPHORIN 2-OXIDES/SULFIDES

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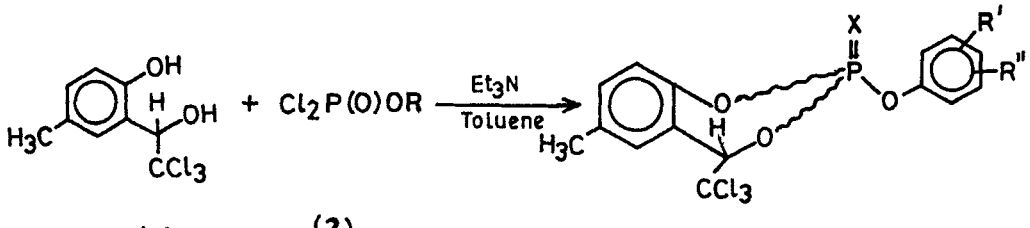
Synthesis of 2-aryloxy-6-methyl-4-trichloromethyl-4H-1,3,2-benzodioxaphosphorin 2-oxides and corresponding 2-sulfides and their IR, ^1H, ^{13}C and ^{31}P NMR spectral analyses were reported. Long-range $^3J_{H-P}$, $^2J_{POC}$ and $^3J_{POCC}$ couplings were determined. An X-ray diffraction analysis of a crystal of 2(2′,6′-dimethylphenoxy)-6-methyl-4-trichloromethyl-4H-1,3,2-benzodioxaphosphorin 2-oxide suggested distorted-boat conformation for the dioxaphosphorin ring with P=O directed away from the ring. Electron impact mass spectra exhibited M^+, $(M—Cl)^+$, $[(M—Cl)—HCl]^+$ and $(M—CCl_3)^+$ as major ions with the dioxaphosphorin ring intact supporting the proposed structures of these esters. Toxicity of some of the compounds against the insect, *P. americana*, was evaluated and their LD_{50} values were reported.

Key words: 2-Aryloxy-6-methyl-4-trichloromethyl-1,3,2-benzodioxaphosphorin 2-oxides/sulfides; NMR and mass spectral analysis; X-ray diffraction of 2(2′,6′-dimethylphenoxy)-6-methyl-4-trichloromethyl-4H-1,3,2-benzodioxaphosphorin 2-oxide; toxicity evaluation.

INTRODUCTION

Large number of organophosphorus esters are being used as pesticides[1] and insecticides.[2] Synthesis of 2-aryloxy-6-methyl-4-trichloromethyl-4H-1,3,2-benzodioxaphosphorin 2-oxides/sulfides (**3**) was accomplished in our endeavour to develop potential pesticides in continuation of our work.[3] Structures of the compounds was determined by spectral studies and X-ray diffraction study of **3f**.



(1) (2) (3)

[R′ and R″ = H, CH_3, or Cl]

	R	X		R	X
3a	C_6H_5	O	**3i**	C_6H_5	S
3b	2′-$H_3CC_6H_4$	O	**3j**	2′-$H_3CC_6H_4$	S
3c	3′-$H_3CC_6H_4$	O	**3k**	3′-$H_3CC_6H_4$	S
3d	4′-$H_3CC_6H_4$	O	**3l**	4′-$H_3CC_6H_4$	S
3e	2′,3′-$(H_3C)_2C_6H_3$	O	**3m**	2′,3′-$(H_3C)_2C_6H_3$	S
3f	2′,6′-$(H_3C)_2C_6H_3$	O	**3n**	2′,6′-$(H_3C)C_6H_3$	S
3g	2′-ClC_6H_4	O	**3o**	2′-ClC_6H_4	S
3h	4′-ClC_6H_4	O	**3p**	4′-ClC_6H_4	S

RESULTS AND DISCUSSION

The cyclization of 2(2,2,2-trichloro-1-hydroxyethyl)-4-methylphenol[4] (**1**) with aryl phosphorodichloridates/aryl phosphorothioicdichlorides (**2**) occurred in the presence of triethylamine within 4–7 hours in dry toluene at 40–50°C. Filtration of the triethylamine hydrochloride followed by evaporation of the solvent produced the crude solids of **3**. The residues were recrystallized, after washing with water, from 2-propanol as colourless crystals. Physical properties and characteristic IR frequences for νP=O,[5] νP=S,[6] νP—O—C (arom),[7,8] and νP—O—C (aliph)[7] are recorded in Table I.

The ^{1}H NMR spectra of **3a–3p** (Table II) showed characteristic doublets in the region δ 5.74–5.81 (J = 17.0–18.5 Hz) for methine proton [H(4)] due to the long-range coupling [$^3J_{H—P}$] between phosphorus and methine proton. The aromatic protons of benzodioxaphosphorin moieties and P-aryloxy groups resonated as complex multiplets in the region δ 7.04–7.37.

The ^{13}C chemical shifts (Table III) were interpreted based on additivity rules, C—P couplings and intensity of signals. The carbons C(4), C(8), C(9) and C(10) experienced coupling with phosphorus. Low-intensity doublets at 88.7–88.9 ppm [$^2J_{POC(4)}$ = 9.3–10.0 Hz][3b] and 147.1–147.6 ppm [$^2J_{POC(9)}$ = 6.0–7.1 Hz][9] were assigned to C(4) and C(9) which bear oxygen atoms. Doublets in the regions 119.8–120.2 ppm [$^3J_{POCC(8)}$ = 6.9–7.3 Hz] and 117.0–118.0 ppm [$^3J_{POCC(10)}$ = 3.4 Hz] were attributed to C(8) and C(10).[10] The methyl groups attached C(6) carbon resonated at 134.3–134.7 ppm while C(5) and C(7) signals occurred around 132.8 ppm and 131.0 ppm respectively.

A doublet at 147.9–149.8 ppm [$^2J_{POC(1')}$ = 7.0–7.9 Hz] was ascribed to C(1′).[11] Both C(2′) and C(6′) exhibited coupling to phosphorus with $^3J_{POCC(2')}$ = 4.3–6.7 Hz and $^3J_{POCC(6')}$ = 4.3–4.9 Hz respectively.[10] An upfield shift of about 4 ppm for the methyl group attached to C(2′) in **3b** and **3j** was attributed to its ν-interaction with the exocyclic oxygen atom [9,12,13] whereas 8 ppm for the C(2′) in **3e** and **3n** was due to its interaction with both exocyclic oxygen atom and C(3′) methyl group.[3c]

The ^{31}P NMR signals occurred in the ranges from −17.1 to −18.1 ppm in **3a–3h** and from +52.1 to +52.8 ppm in **3i–3p**.

TABLE I

Physical data and IR bands of **3**

Compd.[a]	MF	M.P (°C)	Yield (%)	Found (%) (Required)		IR (ν_{max}), cm^{-1}				
								P—O—C(arom)		
				C	H	P=O	P=S	O—C	P—O	P—O—C(aliph)
3a	$C_{15}H_{12}Cl_3O_4P$	120–21	48	45.69 (45.78)	3.10 (3.07)	1305	—	1180	980	1140
3b	$C_{16}H_{14}Cl_3O_4P$	139–40	52	47.14 (47.15)	3.42 (3.46)	1310	—	1180	985	1150
3c	$C_{16}H_{14}Cl_3O_4P$	145–46	55	47.17 (47.15)	3.49 (3.46)	1300	—	1170	975	1140
3d	$C_{16}H_{14}Cl_3O_4P$	141–42	53	47.16 (47.15)	3.48 (3.46)	1305	—	1185	980	1145
3e	$C_{17}H_{16}Cl_3O_4P$	122–23	56	48.40 (48.43)	3.82 (3.83)	1300	—	1170	990	1130
3f	$C_{17}H_{16}Cl_3O_4P$	140–41	54	48.41 (48.43)	3.86 (3.83)	1300	—	1180	980	1130
3g	$C_{15}H_{11}Cl_4O_4P$	128–29	58	42.05 (42.09)	2.63 (2.59)	1310	—	1190	990	1135
3h	$C_{15}H_{11}Cl_4O_4P$	152–53	52	42.04 (42.09)	2.52 (2.59)	1305	—	1185	970	1130
3i	$C_{15}H_{12}Cl_3O_3PS$	100–01	50	44.01 (43.98)	3.00 (2.95)	—	750	1190	960	1120
3j	$C_{16}H_{14}Cl_3O_3PS$	130–31	52	45.32 45.36)	3.28 (3.33)	—	740	1185	955	1130
3k	$C_{16}H_{14}Cl_3O_3PS$	137–38	48	45.31 (45.36)	3.36 (3.33)	—	740	1170	950	1120
3l	$C_{16}H_{14}Cl_3O_3PS$	132–33	53	45.39 (45.36)	3.38 (3.33)	—	750	1180	950	1135
3m	$C_{17}H_{16}Cl_3O_3PS$	116–17	47	46.59 (46.65)	3.63 (3.68)	—	735	1190	960	1125
3n	$C_{17}H_{16}Cl_3O_3PS$	136–37	55	46.60 (46.65)	3.71 (3.68)	—	750	1185	950	1130
3o	$C_{15}H_{11}Cl_4O_3PS$	138–39	52	40.51 (40.57)	2.57 (2.50)	—	740	1190	960	1120
3p	$C_{15}H_{11}Cl_4O_3PS$	152–53	57	40.50 (40.57)	2.55 (2.50)	—	750	1180	965	1125

[a]Compounds recrystallized from 2-propanol.

TABLE II

^1H and ^{31}P NMR data of **3**

Compd.	^1H NMR ($DCCl_3$/TMS), δ				^{31}P NMR, ppm ($DCCl_3$/85%H_3PO_4)
	H(4)[a]	Ar-H	6-CH_3	R',R''-H	
3a	5.76(17.7)	7.05–7.31 m(8H-Ar)	2.38 s	—	−17.21
3b	5.74(17.0)	7.04–7.34 m(7H-Ar)	2.39 s	2.13 s(3H—CH_3)	−17.71
3c	5.75(17.3)	7.03–7.32 m(7H-Ar)	2.37 s	2.25 s(3H—CH_3)	—[b]
3d	5.74(17.1)	7.04–7.35 m(7H-Ar)	2.40 s	2.27 s(3H—CH_3)	−17.23
3e	5.80(18.3)	7.07–7.35 m(6H-Ar)	2.38 s	2.34 s(6H—CH_3)	−17.31
3f	5.81(18.5)	7.06–7.36 m(6H-Ar)	2.39 s	2.47 s(6H—CH_3)	−17.16
3g	5.75(17.6)	7.05–7.35 m(7H-Ar)	2.39 s	—	−18.12
3h	5.74(17.4)	7.06–7.35 m(7H-Ar)	2.38 s	—	—[b]
3i	5.78(17.5)	7.08–7.34 m(8H-Ar)	2.39 s	—	+52.53
3j	5.76(17.1)	7.09–7.36 m(7H-Ar)	2.39 s	2.15 s(3H—CH_3)	+52.61
3k	5.74(17.5)	7.08–7.35 m(7H-Ar)	2.38 s	2.23 s(3H—CH_3)	—[b]
3k	5.78(17.2)	7.09–7.34 m(7H-Ar)	2.41 s	2.28 s(3H—CH_3)	+52.84
3m	5.76(18.3)	7.10–7.36 m(6H-Ar)	2.38 s	2.36 s(6H-CH_3)	+52.09
3n	5.77(18.1)	7.10–7.34 m(6H-Ar)	2.39 s	2.46 s(6H-CH_3)	+52.17
3o	5.81(17.6)	7.11–7.37 m(7H-Ar)	2.39 s	—	+52.73
3p	5.80(17.4)	7.11–7.38 m(7H-Ar)	2.38 s	—	—[b]

[a]Data in parentheses are coupling constants J_{PH} (in Hz).
[b]Not recorded; **3c**, **3h**, **3k** and **3p** are positional isomers of **3b**, **3g**, **3j** and **3o** respectively.

Electron impact mass spectra, were recorded for some members of **3**, showed $(M + 6)^+$ (low intensity), $(M + 4)^+$ and $(M + 2)^+$ ions with intensities expected for three chlorine atoms, and $(M + 8)^+$ (low intensity), $(M + 6)^+$, $(M + 4)^+$ and $(M + 2)^+$ ions for four chlorine atoms (**3g** and **3o**) along with M^+ ions[16] with abundances 7.9–42.4% confirming the proposed structures. The characteristic daughter ion (M—CCl_3), 2-aryloxy-6-methyl-4H-1,3,2-benzodioxaphosphorin 2-oxide/sulfide ion, formed base peak in all spectra. Other common principal ions are $(M—Cl)^+$ and $[(M—Cl)—HCl]^+$ containing benzodioxaphosphorin ring system supporting the structures of **3**. The daughter ions are ascertained by the high resolution electron impact mass spectral data of **3b**.

The structure of crystalline **3f** was determined by X-ray diffraction analysis in an effort to establish the conformation of the six-membered heterocyclic system. Needle like crystals were obtained from 2-propanol. A view of the molecule down the "a" axis in Figure 1 shows the atomic designation. Bond lengths and bond angles, excluding hydrogen, are given in Tables V and VI respectively. The P=O bond length [1.541(2)Å], and the P—O single bond lengths are equal within the limits of error with an average value of 1.572(2)Å. The C(arom)—O bond length is 1.401(3)Å.[17–19] It was observed that there is no significant difference between the endocyclic P—O—C angles [120.1(1)° and 126.4(1)°] and the corresponding exocyclic angle [122.4(1)°]. The difference between the two endocyclic P—O—C angles is a consequence of the fusion of benzene ring and bonding of CCl_3 group to the heterocyclic ring.

A least-square plane passing through P(2), O(3), C(9) and C(10) atoms of the heterocyclic ring shows boat conformation to the benzodioxaphosphorin ring with a maximum deviation of 0.018(2)Å for C(10) atom whereas the atoms O(1)

TABLE III

^{13}C NMR data[a] for members of **3**[b] (ppm from TMS)

Carbon atom	**3a**	**3b**	**3d**	**3e**	**3f**	**3g**	**3i**	**3j**	**3l**	**3n**	**3o**
C(4)	89.3	89.4	89.3	88.8	88.9	89.3	88.7	88.8	88.8	88.9	88.7
	(8.2)	(8.5)	(8.4)	(8.2)	(8.1)	(7.9)	(9.3)	(9.3)	(8.7)	(9.6)	(9.7)
C(5)	132.8	132.8	132.8	132.7	132.7	132.8	132.7	132.8	132.6	132.8	133.0
C(6)	134.5	134.5	134.6	134.3	134.3	134.5	134.5	134.5	134.4	134.5	134.7
C(7)	131.0	130.9	131.0	130.7	130.7	131.0	129.8	129.9	129.9	130.0	129.8
C(8)	119.3	119.3	119.4	119.6	119.7	119.3	119.8	119.8	119.8	120.0	120.0
	(6.3)	(6.5)	(7.1)	(7.0)		(6.4)	(6.9)	(6.3)	(7.2)	(7.1)	(7.1)
C(9)	148.1	148.2	148.1	147.8	147.8	146.6	147.1	147.4	147.1	147.2	147.1
	(7.6)	(7.8)	(7.8)	(6.5)	(6.0)	(7.2)	(7.1)	(7.3)		(6.2)	(6.0)
C(10)	117.0	117.1	117.1	117.5	117.4	117.0	117.1	117.7	117.7	117.8	118.0
	(3.4)		(3.2)	(3.3)	(3.5)	(3.3)	(3.5)	(3.1)		(3.3)	(3.3)
C(1′)	149.4	148.6	147.9	148.4	148.2	148.1	149.8	148.6	148.2	148.5	148.8
	(7.9)	(7.4)	(7.7)	(6.8)		(7.2)	(7.9)	(7.3)	(7.8)	(7.5)	(7.0)
C(2′)	120.3	129.0	120.2	129.0	129.7	130.8	120.5	129.2	120.4	130.1	130.8
		(6.7)		(3.7)	(4.3)		(3.2)		(2.7)		
C(3′)	124.9	131.4	130.0	138.3	128.9	128.1	129.9	131.2	130.9	129.8	128.4
C(4′)	124.7	125.5	134.4	125.6	125.6	126.7	125.1	125.4	133.9	125.6	126.3
C(5′)	129.9	127.1	130.0	127.2	128.9	125.4	129.9	127.2	130.0	129.8	125.1
C(6′)	120.3	119.6	120.2	117.3	129.7	121.8	120.5	120.0	120.4	130.1	121.4
		(3.6)	(4.1)		(4.3)		(3.2)		(2.7)		
4-CCl_3	99.1	99.1	99.0	99.0	99.1	99.1	99.7	99.8	99.7	99.8	99.9
6-CH_3	20.8	20.7	20.8	20.8	20.7	20.8	20.9	20.9	20.9	20.8	20.9
2′-CH_3	—	15.8	—	—	—	—	—	16.1	—	—	—
4′-CH_3	—	—	19.8	—	—	—	—	—	20.3	—	—
2′,3′-CH_3	—	—	—	13.2	—	—	—	—	—	—	—
				20.7							
2′,6′-CH_3	—	—	—	—	17.0	—	—	—	—	17.3	—

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

[b]Data not recorded for **3c**, **3h**, **3k**, **3m** and **3p** since they are positional isomers of **3b**, **3g**, **3j**, **3n** and **3o** respectively.

TABLE IV

Mass spectral data[a] for members of **3**[b]

Compd.	M^+	$(M—Cl)^+$	$[(M—Cl)—HCl]^+$	$(M—CCl_3)^+$
3a	392(22.7)	357(3.1)	321(54.6)	275(100)
3b	406(10.3)	371(8.9)	335(41.2)	289(100)
3d	406(7.9)	371(6.3)	335(45.9)	289(100)
3e	420(12.5)	385(0.7)	349(34.8)	303(100)
3f	420(8.2)	385(0.9)	349(30.6)	303(100)
3g	426(18.1)	391(19.7)	355(39.8)	309(100)
3i	408(42.4)	373(38.4)	337(58.4)	291(100)
3j	422(10.8)	387(1.8)	351(1.2)	305(100)
3m	436(5.3)	—	365(0.7)	319(100)
3o	442(11.5)	407(2.6)	371(0.4)	325(100)

[a]Data in parentheses are relative abundance (%).

[b]Data not recorded for **3c**, **3h**, **3k**, **3l**, **3n** and **3p** since they are parallel to **3b**, **3g**, **3i**, **3j**, **3m** and **3o** respectively.

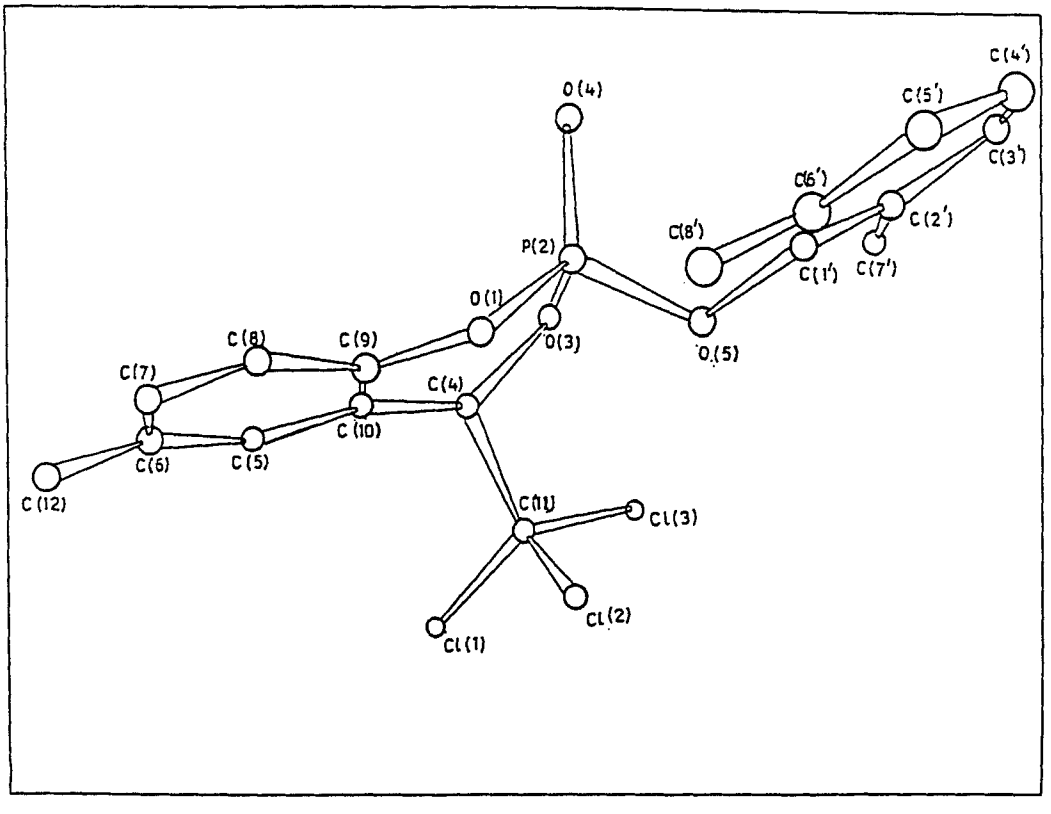


FIGURE 1 Perspective view of the molecule, **3f**.

TABLE V

Bond lengths (in Å) involving non-hydrogen atoms with e.s.d's in parentheses

Cl(1)	—C(11)	1.764(3)	C(4)	—C(11)	1.546(3)
Cl(2)	—C(11)	1.777(3)	C(5)	—C(10)	1.397(3)
Cl(3)	—C(11)	1.752(2)	C(6)	—C(5)	1.390(4)
P(2)	—O(4)	1.451(2)	C(6)	—C(12)	1.500(3)
P(2)	—O(1)	1.576(2)	C(7)	—C(6)	1.392(3)
P(2)	—O(3)	1.573(2)	C(10)	—C(4)	1.506(3)
P(2)	—C(5)	1.566(1)	C(1′)	—C(2′)	1.387(4)
O(1)	—C(9)	1.401(3)	C(1′)	—C(6′)	1.388(4)
O(3)	—C(4)	1.442(3)	C(2′)	—C(3′)	1.395(3)
O(5)	—C(1)	1.417(3)	C(2′)	—C(7′)	1.502(4)
C(8)	—C(7)	1.379(3)	C(3′)	—C(4′)	1.375(5)
C(9)	—C(8)	1.384(3)	C(4′)	—C(5′)	1.370(5)
C(9)	—C(10)	1.380(2)	C(5′)	—C(6′)	1.382(5)
			C(6′)	—C(8′)	1.505(4)

TABLE VI

Bond angles (in deg.) involving non-hydrogn atoms with e.s.d's in parentheses

O(1)	—P(2)	—O(5)	101.5(1)	C(8)	—C(9)	—C(10)	122.9(2)
O(1)	—P(2)	—O(3)	105.0(1)	C(9)	—C(8)	—C(7)	118.1(2)
O(1)	—C(9)	—C(10)	120.0(2)	C(9)	—C(10)	—C(4)	121.2(2)
O(1)	—C(9)	—C(8)	117.1(2)	C(9)	—C(10)	—C(5)	117.4(2)
O(3)	—P(2)	—O(5)	105.3(1)	C(10)	—Cl(4)	—C(11)	115.4(2)
O(3)	—C(4)	—C(10)	112.1(2)	Cl(1)	—Cl(11)	—C(4)	111.6(2)
O(3)	—C(4)	—C(11)	107.9(2)	Cl(1)	—Cl(11)	—Cl(3)	108.9(1)
O(4)	—P(2)	—O(5)	114.9(1)	Cl(1)	—C(11)	—Cl(2)	109.1(1)
O(4)	—P(2)	—O(3)	112.7(1)	Cl(2)	—C(11)	—C(4)	108.9(2)
O(4)	—P(2)	—O(1)	116.1(1)	Cl(2)	—C(11)	—Cl(3)	108.8(1)
O(5)	—C(1)	—C(6′)	118.6(2)	Cl(3)	—C(11)	—C(4)	109.5(2)
O(5)	—C(1′)	—C(2′)	117.2(2)	C(1′)	—C(6′)	—C(8′)	121.9(2)
P(2)	—O(1)	—C(9)	120.1(1)	C(1′)	—C(2′)	—C(7′)	121.0(2)
P(2)	—O(3)	—C(4)	126.4(1)	C(1′)	—C(2′)	—C(3′)	116.3(2)
P(2)	—O(5)	—C(1′)	122.4(1)	C(1′)	—C(6′)	—C(5′)	116.6(2)
C(5)	—C(10)	—C(4)	121.4(2)	C(2′)	—C(1′)	—C(6′)	124.0(2)
C(5)	—C(6)	—C(12)	121.5(2)	C(2′)	—C(3′)	—C(4′)	121.4(2)
C(6)	—C(5)	—C(10)	121.6(2)	C(3′)	—C(2′)	—C(7′)	122.7(2)
C(7)	—C(6)	—C(5)	118.3(2)	C(3′)	—C(4′)	—C(5′)	119.8(3)
C(7)	—C(6)	—C(12)	120.2(2)	C(4′)	—C(5′)	—C(6′)	121.9(3)
C(8)	—C(7)	—C(6)	121.7(2)	C(5′)	—C(6′)	—C(8′)	121.6(2)

[−0.416(2)Å] and C(4) [−0.282(2)Å] are puckered to one side of the ring. The puckering parameters calculated for the six-membered 1,3,2-dioxaphosphorin ring are $q_2 = 0.405(2)$, $q_3 = 0.045(2)$, $\phi_2 = 56.4(3)$, QT = 0.407(2) and $\theta_2 = 83.7(3)°$ respectively. On the other hand, the conformation of the six-membered heterocyclic ring when described with respect to the fused benzene ring, shows that C(9) · · · C(4) and O(1) atoms are in a plane while P(2) and O(3) atoms are puckered to one side of this plane. The C(4)—C(11) bond is vertical to this plane and the geometry at C(11) atom is a regular tetrahedron. At P(2) the O(4) atom is axial whereas 2′,6′-dimethylphenoxy group is equatorial to 1,3,2-dioxaphosphorin ring. The molecule

TABLE VII

Positional parameters and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	x	y	z	B_{eq}(Å^2)
Cl(1)	0.2820(1)	0.3358(0)	0.1750(1)	5.48(2)
Cl(2)	0.2502(1)	0.3877(1)	−0.1464(1)	6.50(3)
Cl(3)	0.1159(1)	0.2707(0)	−0.0607(1)	6.69(3)
P(2)	0.1785(0)	0.5110(0)	0.2380(1)	2.72(1)
O(1)	0.1471(1)	0.4553(1)	0.3594(2)	3.61(4)
O(3)	0.1434(1)	0.4753(1)	0.0707(2)	3.23(4)
O(4)	0.1303(1)	0.5822(1)	0.2473(2)	3.52(4)
O(5)	0.3110(1)	0.5081(1)	0.2715(2)	3.24(4)
C(4)	0.0895(2)	0.4063(1)	0.0386(2)	2.82(5)
C(5)	−0.0721(2)	0.3402(1)	0.1328(3)	3.13(5)
C(6)	−0.1347(2)	0.3208(1)	0.2493(3)	3.34(6)
C(7)	−0.1024(2)	0.3485(1)	0.4009(3)	3.69(6)
C(8)	−0.0100(2)	0.3933(1)	0.4373(3)	3.48(7)
C(9)	0.0516(2)	0.4098(1)	0.3186(2)	2.88(6)
C(10)	0.0235(2)	0.3842(1)	0.1661(2)	2.76(5)
C(11)	0.1807(2)	0.3522(1)	0.0048(3)	3.85(6)
C(12)	−0.2336(2)	0.2704(1)	0.2151(4)	4.55(8)
C(1′)	0.3780(2)	0.5678(1)	0.3319(3)	2.81(5)
C(2′)	0.4248(2)	0.6092(1)	0.2243(3)	3.58(6)
C(3′)	0.4960(2)	0.6651(1)	0.2872(4)	4.61(8)
C(4′)	0.5186(2)	0.6777(2)	0.4474(4)	5.35(9)
C(5′)	0.4700(2)	0.6351(2)	0.5484(3)	5.01(8)
C(6′)	0.4001(2)	0.5781(1)	0.4945(3)	3.49(5)
C(7′)	0.4011(3)	0.5927(2)	0.0504(3)	5.48(9)
C(8′)	0.3515(2)	0.5294(2)	0.6067(3)	4.69(7)

TABLE VIII

Selected torsion angles (in deg.) with e.s.d's. in parentheses

O(1)	—C(9)	—C(10)	—C(4)	−3.9(3)
O(1)	—P(2)	—O(5)	—C(1′)	−116.0(2)
O(1)	—P(2)	—O(3)	—C(4)	2.5(2)
O(3)	—P(2)	—O(5)	—C(1′)	134.7(2)
O(3)	—P(2)	—O(1)	—C(9)	−34.5(2)
O(4)	—P(2)	—O(3)	—C(4)	−124.8(2)
O(5)	—P(2)	—O(1)	—C(9)	−144.0(2)
P(2)	—O(1)	—C(9)	—C(8)	−143.5(2)
P(2)	—O(1)	—C(9)	—C(10)	37.4(3)
P(2)	—O(3)	—C(4)	—C(11)	−102.9(2)
P(2)	—O(3)	—C(4)	—C(10)	25.1(2)
P(2)	—O(5)	—C(1′)	—C(2′)	−99.2(2)
P(2)	—O(5)	—C(1′)	—C(6′)	85.7(2)
C(5)	—C(10)	—C(4)	—C(11)	−85.4(3)
C(9)	—C(10)	—C(4)	—C(11)	98.1(2)
C(10)	—C(4)	—C(11)	—Cl(3)	61.7(2)
C(10)	—C(4)	—C(11)	—Cl(2)	−179.4(2)
C(10)	—C(4)	—C(11)	—Cl(1)	−58.9(2)

TABLE IX

Least-square plane for the heterocyclic ring

Atom	Deviation	Std. Deviation
P(2)*	0.0007	0.0005
C(9)*	−0.0172	0.0022
C(10)*	0.0180	0.0022
O(3)*	−0.0079	0.0016
O(1)	−0.4158	0.0016
C(4)	−0.2821	0.0022

a = −0.7699(4); b = 0.6124(5); c = −0.1796(9); d = 4.0637(50)

TABLE X

Atomic co-ordinates (in Å) of hydrogen atoms

Atom	x	y	z
$H(C_4)$	0.0373	0.4107	−0.0661
$H(C_5)$	−0.0945	0.3230	0.0264
$H(C_7)$	−0.1477	0.3350	0.4808
$H(C_8)$	0.0137	0.4144	0.5375
$H(C_{12})$	−0.2049	0.2179	0.2372
$H'(C_{12})$	−0.2664	0.2687	0.1099
$H''(C_{12})$	−0.2928	0.2819	0.2689
$H(C_3')$	0.5267	0.6962	0.2167
$H(C_4')$	0.5694	0.7208	0.4875
$H(C_5')$	0.4895	0.6429	0.6673
$H(C_7')$	0.4425	0.6262	−0.0102
$H'(C_7')$	0.3198	0.5956	0.0044
$H''(C_7')$	0.4211	0.5421	0.0271
$H(C_8')$	0.3123	0.4879	0.5673
$H'(C_8')$	0.2999	0.5545	0.6591
$H''(C_8')$	0.4108	0.5071	0.6851

exists in minimum energy conformation by puckering the CCl_3 group opposite to that of phosphoryl oxygen atom. The phenyl groups [C(9) · · · C(10) and C(1′) · · · C(6′)] are planar and the atoms O(5), C(7′) and C(8′) are in the plane of C(1′) · · · C(6′) atoms with a maximum deviation for C(5) [0.013(2)Å] atom. The phenyl groups are oriented at a dihedral angle of 19.4(1)°. The packing of the molecules viewed down "b" axis are shown in Figure 2.

TOXICITY EVALUATION

Different concentrations of selected test compounds **3a**, **3d**, **3h**, **3i**, **3l**, and **3p** were prepared in acetone, and the solutions were sprayed onto the cuticle 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[20] probit analysis treatment to derive the graphs, namely: (1) log concentration versus percent kill and (2) log concentration versus probit kill, to obtain LD_{50} values. The LD_{50} values of the

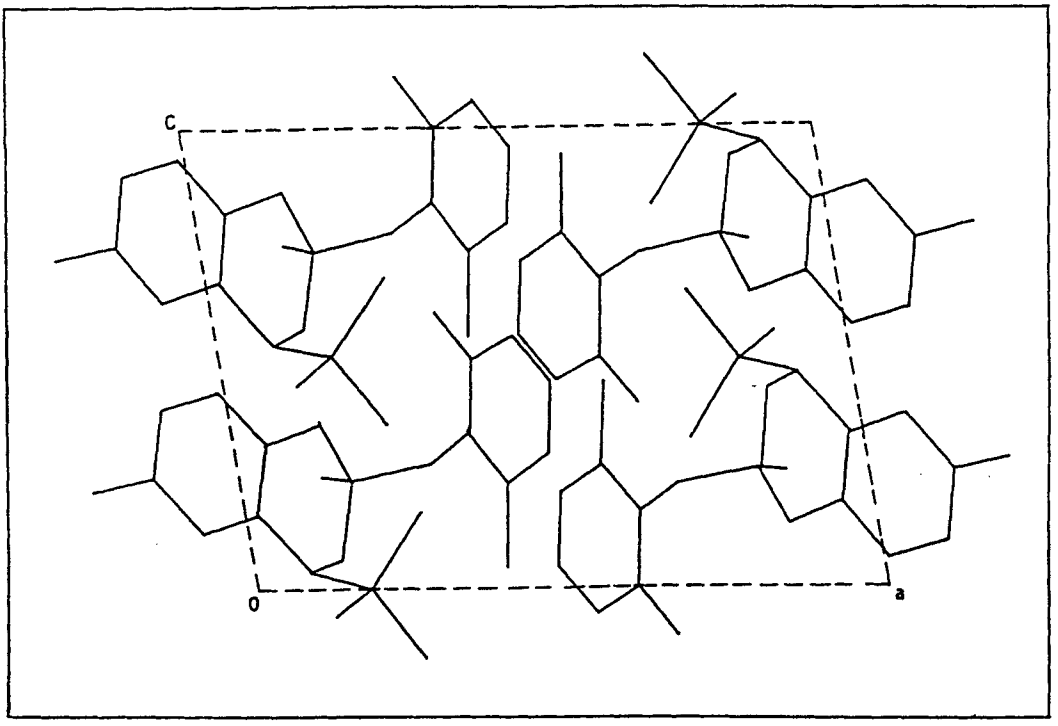


FIGURE 2 Packing of the molecules in the unit cell viewed down "b" axis.

selected test compounds **3a**, **3d**, **3h**, **3i**, **3l**, and **3p** were found be to 14.73, 12.34, 9.67, 20.7, 18.05, and 16.52 mg/kg (data taken from the above cited graphs), respectively.

EXPERIMENTAL

The melting points were uncorrected. Elemental analyses and mass spectra were recorded by RSIC, Central Drug Research Institute, Lucknow, India. IR spectra were recorded as KBr pellets on a Perkin-Elmer 683 spectrophotometer, ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian XL-300 spectrometer operating at 299.9 MHz for ^{1}H, 75.43 MHz for ^{13}C, and 121 MHz for ^{31}P. All NMR data were taken on $DCCl_3$ solutions and were referenced from TMS (^{1}H and ^{13}C, δ or ppm) or 85% H_3PO_4 (^{31}P, ppm).

2(2'-methylphenoxy)-6-methyl-4-trichloromethyl-4H-1,3,2-benzodioxaphosphorin 2-oxide (**3b**). A solution of 2-methylphenylphosphorodichloridate (**2b**, 2.25 g, 0.01 mol) in dry toluene (20 ml) was added dropwise over a period of 30 minutes to a stirred solution of 2-(2,2,2-trichloro-1-hydroxyethyl)-4-methylphenol (**1**, 2.50 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in dry toluene (80 ml). After completion of the addition, the stirring was continued for 5 hours at 40–50°C. Progress of the reaction was followed by TLC analyses. Solid triethylamine hydrochloride was filtered and the solvent from the filtrate was evaporated under reduced pressure. The crude product was washed with water and recrystallized form 2-propanol as colourless crystals of **3b**, yield 2.56 g (54%), mp 138–39°C. All members of **3** were synthesized by the same procedure.

Crystal Structure Determination. A colourless crystal with dimensions 0.5 × 0.3 × 0.15 mm of **3f** was grown from a solution of 2-propanol and was needle-like in shape. It was used for data collection with

preliminary crystal data being determined by Weissenberg technique. Accurate cell dimensions were subsequently refined from a least-squares procedure using 25 medium angle reflections ($35° < \theta < 45°$) with a Enraf-Nonius CAD-4 diffractometer.

The crystal data were: $C_{17}H_{16}Cl_3O_4P$, MW = 421.644, monoclinic, space group $P2_1/c$, a = 11.969(1), b = 18.58(1), c = 8.568(1) Å, β = 99.38(1)°, Z = 4, D_m = 1.491 g/cm^3, D_x = 1.490 g/cm^3, F (000) = 864, V = 1880.2(3) Å^3, μ(MoK α) = 5.90 cm^{-1}, λ (MoK α) = 0.71069Å.

A total of 4835 independent reflections were taken by $\omega/2\theta$ scan technique with $0 \leq 2\theta \leq 54°$. After application of Lorentz and Polarization correction, 3344 reflections were found significant with $1 \geq 3\sigma(1)$. No absorption corrections were applied. The structure was solved by direct methods using SHELX-86.[21] The structure was refined to R-index 0.068 by a least-square method using SHELX-76[22] where upon all hydrogen atoms were located from a difference Fourier map. Further anisotropic refinement leads to a final R-value of 0.0432 and R_w = 0.0509 using the weighting scheme = 2.2014/(σ^2F + 0.000551 F^2). The final difference Fourier map showed no significant features with a maximum peak height of 0.40e/Å^3. The atomic scattering factors used for the non-hydrogen atoms were from Cromer and Weber.[23] Table VII lists the final positional parameters of non-hydrogen atoms.

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