Synthesis and Characterization of Some 2,10-Dichloro-6-alkoxydibenzo[*d*,*g*][1,3,6,2]dioxathiaphosphocin 6-Oxides

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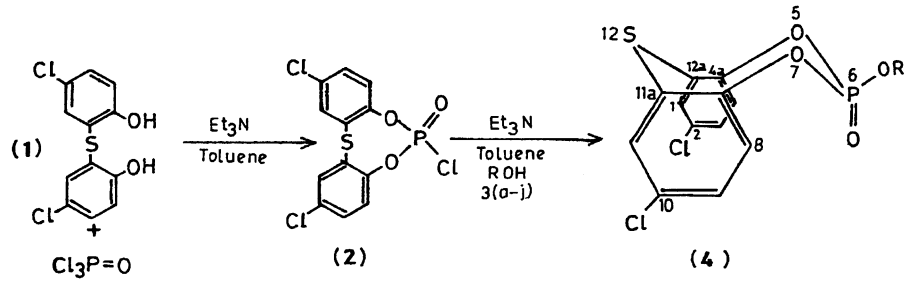
The syntheses of 2,10-dichloro-6-alkoxydibenzo[*d*,*g*][1,3,6,2]dioxathiaphosphocin 6-oxides are described. Their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectral characteristics are reported. Long-range couplings ($^{2}J_{POC}$ and $^{3}J_{POCC}$) between phosphorus and carbons were observed. An X-ray diffraction analysis of a crystal of 2,10-dichloro-6-ethoxydibenzo[*d*,*g*][1,3,6,2]dioxathiaphosphocin 6-oxide indicated a boat-chair conformation to the dioxathiaphosphocin ring with the phosphoryl oxygen in axial and the ethoxy group in equatorial orientations. The molecule possesses a symmetry of the mirror plane passing through the sulfur, phosphorus, phosphoryl oxygen, and ethoxy group.

Keen interest has recently been evinced concerning the synthesis of phosphate esters in view of their multifaceted applications as pesticides,[1] flame retardants and lubricants.[2] In our attempts to develop safe, selective and effective pesticides which are specifically toxic only on the target pests, but not on mammals, a series of 2,10-dichloro-6-alkoxydibenzo[*d*,*g*]-[1,3,6,2]dioxathiaphosphocin 6-oxides (**4**) were prepared and characterized by spectral and X-ray crystallographic investigations on 2,10-dichloro-6-ethoxydibenzo[*d*,*g*][1,3,6,2]dioxathiaphosphocin 6-oxide (**4b**).

Results and Discussion

The reaction of 4,4′-dichloro-2,2′-thiodiphenol (**1**)[3] with phosphoryl chloride in the presence of triethylamine in dry toluene at room temperature produced the monochloride, 2,6,10-trichlorodibenzo[*d*,*g*][1,3,6,2]-dioxathiaphosphocin 6-oxide (**2**). Subsequent reactions of it in situ with various alcohols (**3**) under the same conditions led to the formation of **4** (Scheme 1). The advantage of this method over the conventional method[4] is that there is no necessity to prepare the corrosive and moisture-sensitive alkyl phosphorodichloridates (ROP(O)Cl_2) used for preparing these compounds. The physical properties and IR data[5] are recorded in Table 1.

In the ^{1}H NMR spectra the six aromatic protons (Table 2) of the dibenzodioxathiaphosphocin moieties of **4** showed only three signals, indicating a symmet-



	R		R
4a	CH_3	**4f**	*i*-C_4H_9
4b	C_2H_5	**4g**	*t*-C_4H_9
4c	$H_3C^{3'}CH_2^{2'}CH_2^{1'}$	**4h**	*i*-C_5H_{11}
4d	*i*-C_3H_7	**4i**	*c*-C_6H_{11}
4e	*n*-C_4H_9	**4j**	$C_6H_5CH_2$

Scheme 1.

Table 1. Physical Data and IR Bands of **4**

Compd	MF	Mp °C	Yield[a] %	Found (%) (Calcd) C	Found (%) (Calcd) H	IR (ν_{max}/cm^{-1}) P=O	P–O–C(arom) O–C	P–O–C(arom) P–O	P–O–C (aliph)	C–S–C
4a	$C_{13}H_9O_4Cl_2SP$	164—165[a]	45	43.14 (42.95)	2.64 (2.49)	1300	1250	930	1190	635
4b	$C_{14}H_{11}O_4Cl_2SP$	125—126[a]	42	44.24 (44.54)	3.21 (2.93)	1300	1250	935	1200	640
4c	$C_{15}H_{13}O_4Cl_2SP$	144—145[a]	40	46.45 (46.25)	3.64 (3.44)	1290	1240	930	1200	635
4d	$C_{15}H_{13}O_4Cl_2SP$	148—149[b]	42	46.32 (46.25)	3.72 (3.44)	1290	1240	920	1200	640
4e	$C_{16}H_{15}O_4Cl_2SP$	169—170[b]	40	47.36 (47.38)	3.48 (3.70)	1290	1250	930	1200	640
4f	$C_{16}H_{15}O_4Cl_2SP$	279—280[b]	36	47.40 (47.38)	3.66 (3.70)	1280	1240	930	1200	640
4g	$C_{16}H_{15}O_4Cl_2SP$	275—276[b]	37	47.18 (47.38)	3.74 (3.70)	1300	1250	930	1200	645
4h	$C_{17}H_{17}O_4Cl_2SP$	169—170[b]	33	48.68 (48.65)	4.15 (4.08)	1300	1240	920	1190	635
4i	$C_{18}H_{17}O_4Cl_2SP$	278—279[b]	33	50.12 (50.08)	4.24 (3.97)	1290	1240	930	1190	640
4j	$C_{19}H_{12}O_4Cl_2SP$	253—254[b]	30	52.45 (52.02)	2.96 (2.75)	1280	1250	920	1200	640

a) Crystallized from 2-propanol. b) Crystallized from methanol–toluene (2:1).

Table 2. ^1H and ^{31}P Chemical Shifts (in δ) of **4**[a]

Compd	^1H NMR ($CDCl_3$/TMS) δ H(1, 11)	H(3, 9)	H(4, 8)	R-H	^{31}P NMR[b]
4a	7.68 (2.4)	7.33 (8.5, 2.6)	7.15 (8.4, 1.8)	4.08—4.15 (m, 3H, CH_3)	−11.28
4b	7.69 (2.6)	7.35 (8.7, 2.4)	7.16 (8.8, 1.5)	4.40—4.55 (m, 2H, CH_2) 1.45—1.55 (t, 3H, CH_3)	−12.44
4c	7.69 (2.4)	7.35 (8.6, 2.6)	7.18 (8.6, 1.6)	4.30—4.40 (m, 2H, CH_2) 1.80—1.95 (m, 2H, CH_2) 1.02—1.10 (t, 3H, CH_3)	−12.35
4d	7.68 (2.6)	7.36 (8.6, 2.6)	7.16 (8.5, 1.6)	4.95—5.15 (m, 1H, CH) 1.46—1.56 (d, 6H, CH_3)	−13.38
4e	7.70 (2.6)	7.36 (8.5, 2.6)	7.15 (8.4, 1.6)	4.34—4.46 (m, 2H, CH_2) 1.78—1.88 (q, 2H, CH_2) 1.46—1.58 (s, 2H, CH_2) 0.95—1.05 (t, 3H, CH_3)	−12.33
4f	7.69 (2.5)	7.35 (8.6, 2.4)	7.16 (8.5, 1.5)	4.32—4.89 (m, 2H, CH_2) 1.40—1.60 (m, 1H, CH) 0.80—1.10 (d, 6H, CH_3)	−13.24
4g	7.68 (2.6)	7.36 (8.7, 2.5)	7.15 (8.6, 1.6)	1.45—1.58 (m, 9H, CH_3)	−13.36
4h	7.69 (2.6)	7.34 (8.4, 2.4)	7.15 (8.4, 1.5)	4.40—4.49 (m, 2H, CH_2) 1.70—1.90 (m, 3H, CH_2, CH) 0.97—1.04 (t, 6H, CH_3)	−12.33
4i	7.87 (2.4)	7.49 (7.6, 2.0)	7.33 (8.4, 1.4)	4.75—4.79 (m, 1H, CH) 1.08—2.10 (m, 10H, CH_2)	−12.63
4j	7.75 (2.6)	7.40 (8.3, 2.4)	7.17	5.40—5.51 (d, 2H, CH_2) 6.90—7.33 (m, 5H, Ar-H)	−11.57

a) Data in parentheses are coupling constants J_{H-H} (in Hz). b) Recorded on $CDCl_3$ solutions with external reference 85% H_3PO_4.

rical disposition of the benzene rings.[6] The two doublet of doublets in the regions δ=7.33—7.49 (J=7.6—8.7 and J=2.0—2.6 Hz) and δ=7.15—7.33 (J=8.4—8.8 and J=1.4—1.8 Hz) were assigned to H(3,9) and H(4,8), respectively.[6] Protons H(1,11) resonated as a doublet at δ=7.68—7.87 (J=2.4—2.6 Hz).[6] The signals for the protons of 6-alkoxy groups appeared in the downfield region when compared to the signals of the protons of the corresponding free alcohol protons due to a deshielding effect of the dioxathiaphosphocin 6-oxide ring system. The effect of deshielding decreased with an increase of distance in the alkoxy chain.[7]

The ^{13}C NMR (Table 3) spectra exhibited only six signals for twelve carbons of dibenzodioxathiaphosphocin moieties reinforced the symmetrical disposition of the two benzene rings over the dioxathiaphosphocin ring system.[6,7] Carbons C(4a,7a), C(4,8), and C(11a,12a) experienced coupling to phosphorus. A low-intensity doublet at 150.5—150.6 ppm [$^2J_{POC(4a,7a)}$=8.4—8.8 Hz] was attributed to oxygen-bearing carbons C(4a,7a).[6] Sulfur-bearing carbons C(11a,12a) showed a doublet in the region 127.3—127.4 ppm [$^3J_{POCC(11a,12a)}$=3.9—4.2 Hz] with low intensity. The aromatic carbons C(4,8) have signals at 123.7—123.8 ppm [$^3J_{POCC(4,8)}$=4.6—5.0 Hz].[7] Shifts at 135.6—135.8 ppm and at 131.4—131.6 ppm were ascribed to C(1,11) and C(3,9) respectively.[6] The chlorine-bearing carbons C(2,10) exhibited a low-intensity signal at 131.6—131.9 ppm.[6] Resonances of the C(1′) of P-alkoxy groups occurred downfield (7—10 ppm) when compared to the signals in the corresponding free alcohols.[7] Carbons C(1′) and C(2′) coupled with phosphorus to about the same extent [$^2J_{POC(1')}$= 6.2—6.7 Hz and $^3J_{POCC(2')}$=4.4—7.2 Hz].[7]

The ^{31}P resonances[7] (Table 2) occurred in the range from −11.28 to −13.38 ppm.

The crystal structure of **4b** was determined by an X-ray diffraction analysis to establish the overall molecular geometry of the system. The final atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms are given in Tables 4 and 5, respectively. A view of the molecule along with atom labelling is shown in Fig. 1. The bond lengths and valence angles involving non-hydrogen atoms are given in Table 6. The molecule possesses a mirror symmetry plane passing through the S(12), P(6), O(13), O(14), C(1′), and C(2′) atoms. The P(6)=O(13) [1.455(3) Å] bond length is normal. However, the exocyclic P(6)–O(14) bond length [1.550(2) Å] and the C(1′)–C(2′) bond length [1.435(6) Å] are slightly shorter than the reported values.[8] The mean bond lengths in the benzene ring [1.386(4) Å] and C(arom)–Cl [1.743(3) Å] are in agreement with similar values of 1.379(5) Å and 1.739(3) Å observed in 6-(4-chlorophenoxy)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin 6-sulfide.[9] The bond length of C(4a)–O(5) [1.386(3) Å] is shorter than that reported in cis, trans derivatives of 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin compounds.[10]

X-Ray crystallographic studies showed that the dioxathiaphosphocin ring in **4b** adopts a boat-chair conformation with the phosphoryl oxygen [O(13)] in axial and the ethoxy group in equatorial orientations. A similar conformation has been observed for the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-oxide.[11] It is interesting to note that the bridged sulfur atom in dibenzodioxathiaphosphocins and the bridged methyl-

Table 3. ^{13}C NMR Data (in ppm) of **4**[a)]

Compd	C(1, 11)	C(2, 10)	C(3, 9)	C(4, 8)	C(4a, 7a)	C(11a, 12a)	R
4a	135.8	131.7	131.6	123.7 (5.0)	150.5 (8.4)	127.3 (3.9)	55.78 [1C, C(1′)] (6.2)
4b	135.8	131.6	131.5	123.8 (4.8)	150.5 (8.8)	127.4 (4.0)	66.4 [1C, C(1′)]; 16.3 [1C, C(2′)] (6.4) (6.6)
4c	135.9	131.6	131.5	123.9 (4.9)	150.5 (8.4)	127.4 (4.1)	71.5 [1C, C(1′)]; 23.6 [1C, C(2′)] (6.6) (7.0) 10.0 [1C, C(3′)]
4d	135.8	131.6	131.4	123.9 (4.8)	150.6 (8.4)	127.4 (4.1)	76.1 [1C, C(1′)]; 23.6 [2C, C(2′)] (6.5) (5.3)
4e	135.8	131.6	131.5	123.8 (4.8)	150.6 (8.4)	127.4 (4.2)	69.1 [1C, C(1′)]; 32.1 [1C, C(2′)] (6.6) (7.0) 18.6 [1C, C(3′)]; 13.5 [1C, C(4′)]
4f	135.7	131.6	131.4	123.7 (4.9)	150.5 (8.4)	127.4 (4.1)	75.5 [1C, C(1′)]; 29.0 [1C, C(2′)] (6.7) (7.2) 18.5 [2C, C(3′)]
4h	135.8	131.6	131.4	123.8 (4.8)	150.5 (8.5)	127.3 (3.9)	68.1 [1C, C(1′)]; 38.7 [1C, C(2′)] (6.6) (7.0) 24.4 [1C, C(3′)]; 22.3 [2C, C(4′)]
4i	135.6	131.9	130.4	123.8 (4.6)	150.6 (8.6)	127.3 (4.0)	68.1 [1C, C(1′)]; 32.5 [2C, C(2′, 6′)] (6.3) (4.4) 24.5 [2C, C(3′, 5′)]; 22.7 [1C, C(4′)]

a) Values in parentheses are coupling constants J_{PC} (in Hz).

Table 4. Final Positional Parameters and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms with esd's in Parentheses for Compound **4b**

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
P(6)	0.3651(1)	0.2500(0)	0.2307(1)	3.0(0)
S(12)	0.5550(1)	0.2500(0)	−0.0198(1)	3.6(0)
Cl′	0.7396(0)	0.5798(1)	0.2920(1)	5.1(0)
O(13)	0.3820(2)	0.2500(0)	0.3903(3)	4.3(1)
O(5)	0.4027(1)	0.3620(1)	0.1443(2)	3.3(0)
O(14)	0.2679(1)	0.2500(0)	0.1831(3)	3.5(1)
C(4a)	0.4830(2)	0.4113(2)	0.1789(3)	3.1(1)
C(4)	0.4861(2)	0.5038(2)	0.2802(3)	3.8(1)
C(3)	0.5648(2)	0.5579(2)	0.3139(3)	4.1(1)
C(2)	0.6395(2)	0.5172(2)	0.2439(3)	3.7(1)
C(1)	0.6373(1)	0.4253(2)	0.1420(3)	3.5(1)
C(12a)	0.5582(1)	0.3710(2)	0.1086(2)	3.1(1)
C(1′)	0.2417(3)	0.2500(0)	0.0311(5)	8.8(3)
C(2′)	0.1488(2)	0.2500(0)	0.0116(5)	4.3(1)

Table 5. Anisotropic Thermal Parameters (in Å^2) of Non-Hydrogen Atoms with esd's in Parentheses $U(i,j)\times10^4$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(6)	386(05)	484(06)	286(05)	0(00)	−19(03)	0(00)
S(12)	585(05)	537(06)	232(05)	0(00)	63(03)	0(00)
Cl	610(05)	686(06)	644(05)	91(03)	−113(03)	−208(03)
O(13)	649(16)	693(17)	299(13)	0(00)	−39(11)	0(00)
O(5)	403(08)	475(10)	390(09)	25(07)	−42(06)	12(06)
O(14)	388(11)	599(15)	332(12)	0(00)	7(09)	0(00)
C(4a)	436(11)	405(12)	333(10)	63(08)	11(08)	−14(09)
C(4)	504(13)	443(14)	491(13)	−19(10)	52(10)	72(10)
C(3)	644(16)	412(13)	486(13)	−33(11)	−43(12)	−26(10)
C(2)	536(13)	477(15)	386(11)	110(10)	−43(09)	−71(10)
C(1)	456(12)	509(14)	355(12)	122(09)	21(09)	0(09)
C(12a)	468(12)	413(11)	282(10)	89(08)	25(08)	7(09)
C(1′)	466(21)	2579(98)	314(23)	0(00)	−76(16)	0(00)
C(2′)	471(19)	679(24)	473(20)	0(00)	−76(14)	0(00)

The form of the anisotropic temperature factors is: $T=\exp[-2\pi^2(U_{11}h^2a^{*2}+\cdots+2U_{12}hka^*b^*)]$.

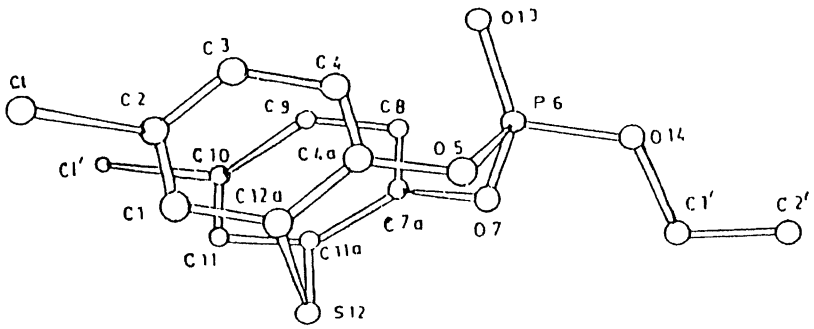


Fig. 1. A perspective view of the molecule for **4b** along with the numbering scheme.

ene group in dibenzodioxaphosphocins have no effect on the conformation of the dioxaphosphocin ring. However, the nature of the substituents on it seems to determine its conformation.

The packing of the molecules viewed down the "c" axis is shown in Fig. 2. The molecule possesses a mirror plane, and is parallel to the (010) plane of the lattice. The crystal structure is stabilized by Van der Waals interactions.

Experimental

The melting points were uncorrected. Microanalyses were performed at Central Drug Research Institute, Lucknow, India. IR (KBr) spectra were recorded on Beckman IR-18A

Table 6. Bond Lengths and Bond Angles for Non-Hydrogen Atoms with esd's in Parentheses for Compound **4b**

a. Bond lengths (in Å)			
P(6)–O(13)	1.455(3)	P(6)–O(5)	1.588(2)
P(6)–O(14)	1.550(2)	S(12)–C(12a)	1.784(2)
Cl–C(2)	1.743(3)	O(5)–C(4a)	1.386(3)
O(14)–C(1′)	1.422(5)	C(4a)–C(4)	1.383(4)
C(4a)–C(2a)	1.390(3)	C(4)–C(3)	1.385(4)
C(3)–C(2)	1.384(4)	C(2)–C(1)	1.381(4)
C(1)–C(12a)	1.391(3)	C(1′)–C(2′)	1.435(6)
b. Bond angles (in deg.)			
O(5)–P(6)–O(14)	102.4(1)	O(13)–P(6)–O(14)	116.3(2)
O(13)–P(6)–O(5)	114.6(1)	P(6)–O(5)–C(4a)	122.1(2)
P(6)–O(14)–C(1′)	122.4(2)	O(5)–C(4a)–C(12a)	120.3 (2)
O(5)–C(4a)–C(4)	118.6(3)	C(4)–C(4a)–C(12a)	121.0(2)
C(4a)–C(4)–C(3)	120.3(3)	C(2)–C(3)–C(4)	118.4(2)
Cl–C(2)–C(3)	118.8(2)	C(3)–C(2)–C(1)	121.9(3)
Cl–C(2)–C(1)	119.2(2)	C(2)–C(1)–C(12a)	119.5(2)
C(4a)–C(12a)–C(1)	118.8(2)	S(12)–C(12a)–C(1)	119.9(2)
O(14)–C(1′)–C(2′)	113.4(3)		

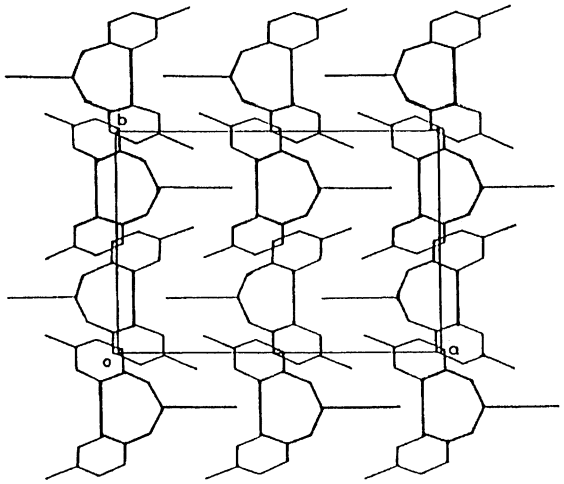


Fig. 2. Packing of the molecule of **4b** in the unit cell viewed down "*c*" axis.

spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz spectrometer on $CDCl_3$ solutions with the chemical shifts (referenced to TMS) reported in δ values or in ppm. The ^{31}P NMR spectra were taken at 121 MHz using a VXR-300 spectrometer on $CDCl_3$ solutions with chemical shifts (referenced to 85% H_3PO_4) reported in ppm.

Preparation of 2,10-Dichloro-6-methoxydibenzo-[*d*, *g*][1,3,6,2]dioxathiaphosphocin 6-Oxide (3a). To a cooled (0—5 °C) and stirred solution of phosphoryl chloride (1.53 g, 0.01 mol) in dry toluene (30 ml), a solution of 4, 4′-dichloro-2,2′-thiodiphenol (**1**, 2.87 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in dry toluene (60 ml) was added dropwise over a period of 30 min. Stirring was continued at room temperature for 4 h. After completion of the formation of the monochloride **2**, as indicated by a TLC analysis of the reaction mixture, it was cooled to 0—5 °C; a solution of triethylamine (1.01 g, 0.01 mol) and absolute methanol (**3a**, 0.32 g, 0.01 mol) in dry toluene (20 ml) was added, and stirring was continued for 2 h at room temperature for completion of the reaction. Triethylamine hydrochloride was separated by filtration and the solvent was removed under reduced pressure. The crude solid was washed with water and recrystallized from 2-propanol as colorless crystals of **3a**; mp 164—165 °C, yield 1.62 g (45%). The same procedure was used for the preparation of **3b**—**3j**.

Crystal Structure Determination. Colorless needle-shaped crystals of **4b** were grown from 2-propanol. The crystal data were: $C_{14}H_{11}O_4PSCl_2$, MW=377.178, orthorhombic, a=15.331(3), b=11.253(2), c=8.973(4) Å, V=1548.0(8) Å^3, space group *Pnma*, Z=4, $F(000)$=768, ρ_0=1.615 and ρ_c=1.618 g cm^{-3}, μ(Cu $K\alpha$)=62.32cm^{-1}. Preliminary cell parameters were obtained from Weissenberg photographs, and a crystal size of 0.42×0.25×0.22 mm was mounted on a Enraf–Nonius CAD 4 diffractometer. Graphite monochromated Cu $K\alpha$ (λ=1.5418 Å) radiation was used. Accurate cell parameters were determined by a least-squares refinement using 20 reflections in the range $45° < 2\theta < 55°$. Intensity data were collected by the $\omega/2\theta$ scan technique with an interval $\Delta\omega = (0.80 + 0.35 \tan\theta)°$, extended by 25% on both sides for background measurements. The intensities of three standard reflections measured periodically during the data collection showed no significant variation. A total of 1736 reflections in the range of $0° < 2\theta < 140°$ were measured (h, 0—18; k, 0—13; l, 0—10), of which 1293 reflections had $I \geq 3\sigma(I)$. Lp corrections were applied, but not absorption correction was made.

The structure was solved by direct methods using the program SHELXS-86.[12] The intensity statistics distribution revealed that the crystal has a centric space group, *Pnma*, possessing a half molecule in an asymmetric unit. A refinement of F by a full-matrix least-squares method using SHELX-76[13] was carried out on the positional and anisotropic thermal parameters of non-hydrogen atoms. All of the hydrogen atoms located from a difference fourier map were included, but not refined. The final refinement converged at R=0.051, R_w=0.059. The final difference Fourier map was featureless with maximum and minimum heights

of 0.3 and -0.5 e Å^{-3}; a secondary extinction correction was not applied. The atomic-scattering factors used for non-hydrogen atoms,[14] hydrogen atoms[15] and anomalous scattering factors[16] were taken from the literature. The Complete $F_o - F_c$ data are deposited as Document No. 68056 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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References

1) a) C. Fest and K. -J. Schmidt, "The Chemistry of Organophosphorus Pesticides," Springer-Verlag, Berlin (1982); b) M. S. Bhatia and J. Pawan, *Experientia*, **32**, 1111 (1976).

2) R. Ismail, German Patent 543539, *Chem. Abstr.*, **83**, 97416 (1975).

3) F. Dunning, B. Dunning, Jr., and W. E. Drake, *J. Am. Chem. Soc.*, **53**, 3466 (1931).

4) C. D. Reddy, K. Anuradha, K. D. Berlin, P. S. Sunthankar, and S. V. Mulekar, *Org. Prep. Proced. Int.*, **22**, 229 (1990).

5) L. C. Thomas, "Interpretation of Infrared Spectra of Organophosphorus Compounds," Heydon & Son, Ltd., London (1974).

6) C. D. Reddy, R. S. N. Reddy, C. N. Raju, M. ElMasri, K. D. Berlin, and S. Subramanian, *Magn. Reson. Chem.*, **29**, 1140 (1991).

7) C. D. Reddy, K. D. Berlin, R. S. Reddy, C. N. Raju, M. ElMasri, and S. Subramanian, *Phosphorus, Sulfur, and Silicon*, **81**, 61 (1993).

8) H. R. Allcock, "Heteroatom Ring System and Polymers," Academic Press, New York (1967).

9) K. Sivakumar, K. Subramanian, S. Natarajan, M. Krishnaiah, and L. Ramamurthy, *Acta Crystallogr., Sect. C*, **C45**, 806 (1989).

10) J. D. Goddard, A. W. Payne, N. Cook, and H. R. Luss, *J. Heterocycl. Chem.*, **25**, 575 (1988).

11) S. Mani Naidu, Ph. D. Dissertation, Sri Venkateswara University, Tirupati, India, 1990.

12) G. M. Sheldrick, "SHELXS-86, a program for the solution of crystal structures from diffractometer data," University of Göttingen, FRG (1986).

13) G. M. Sheldrick, "SHELX-76, a program for the crystal structure determination," University of Cambridge, England (1976).

14) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **A24**, 321 (1968).

15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

16) D. T. Cromer and D. G. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).