Heteroatom Chemistry
Volume 6, Number 5, 1995

Synthesis and Spectral Analysis of 8-Substituted Dinaphtho[2,1-d:1′,2′-g][1,3,6,2]dioxathiaphosphocin 8-Oxides

B. Sankara Reddy, K. Anuradha, and C. Devendranath Reddy*
Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, India

N. Jagadeesh Kumar and M. Krishnaiah
Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

K. Darrell Berlin
Department of Chemistry, Oklahoma State University, Stillwater, OK 74078

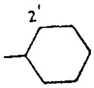
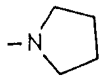
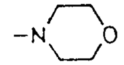
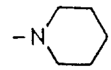
Received 20 August 1994; revised 10 February 1995

ABSTRACT

Synthesis and spectral analysis of several 8-substituted dinaphtho[2,1-d:1′,2′-g][1,3,6,2]dioxathiaphosphocin 8-oxides have been described. An X-ray crystallographic study of 8-(2′,3′- dimethylphenoxy)dinaphtho[2,1 - d:1′,2′-g][1,3,6,2]dioxathiaphosphocin 8-oxide has indicated that, in the solid state, the dioxathiaphosphocin ring is in a distorted-boat-like conformation with the P=O group and bridged S atom directed away from each other. Electron impact mass spectra showed M⁺ and (M-OR)⁺ ions, containing the dioxathiaphosphocin ring system, confirming the structures of the esters. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Since a large number of dioxathiaphosphocins are potential antioxidants and stabilizers in oils and polymers [1], syntheses and spectral analyses of 8-substituted dinaphtho[2,1-d:1′,2′-g][1,3,6,2]dioxathiaphosphocin 8-oxides (**3a–3n**) were accomplished. A distorted boat–chair conformation was suggested for **3** on the basis of an X-ray diffraction study of a crystal of one member, **3e**, of the series.

	R		R
3a	C_6H_5O	3k	
3b	$2'\text{-}H_3CC_6H_4O$		
3c	$3'\text{-}H_3CC_6H_4O$		
3d	$4'\text{-}H_3CC_6H_4O$	3l	
3e	$2',3'\text{-}(H_3C)_2C_6H_3O$		
3f	$2',6'\text{-}(H_3C)_2C_6H_3O$		
3g	$3',4'\text{-}(H_3C)_2C_6H_3O$	3m	
3h	$2'\text{-}H_3C\text{-}4'\text{-}ClC_6H_3O$		
3i	$2'\text{-}ClC_6H_4O$		
3j	C_6H_5	3n	

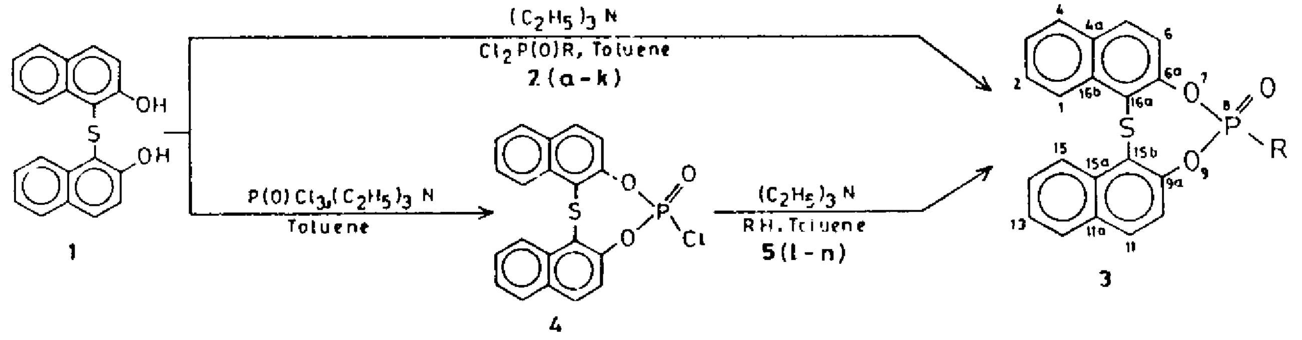
RESULTS AND DISCUSSION

The condensation of bis(2-hydroxy-1-naphthyl)-sulfide (**1**) [2] and aryl phosphoro-dichloridates or phenyl/cyclohexyl phosphonic dichloride (**2**) in equimolar quantities in the presence of triethylamine in dry toluene at 55–65°C produced **3a–3k** (Scheme 1). The compounds **3l–3n** were synthesized using the intermediate acid chloride, 8-chlorodinaphtho [2,1-d:1′,2′-g] [1,3,6,2] dioxathiaphosphocin 8-oxide (**4**). The intermediate was prepared by

---

*To whom correspondence should be addressed.

1042-7163/95/050485-10



SCHEME 1

TABLE 1 Physical Data of 8-Substituted Dinaphtho[2,1-d: 1′, 2′-g][1, 3, 6, 2]-dioxathiaphosphocin 8-Oxides (**3**)

Compound[a] (*Formula*)	*m·p* (°*C*)	*Yield* (%)	*Found* (*Required*) % *C*	*H*	*IR* (*cm*⁻¹) *P=O*	*P–O–Caromatic* *P–O*	*O–C*	^{31}*P NMR*[b] (*CDCl*$_3$)
3a ($C_{26}H_{17}O_4SP$)	186–87	68	68.35 (68.42)	3.84 (3.75)	1300	1235	970	−17.24
3b ($C_{27}H_{19}O_4SP$)	223–24	73	68.81 (68.93)	4.18 (4.07)	1300	1220	970	−17.15
3c ($C_{27}H_{19}O_4SP$)	225–26	74	68.95 (68.93)	4.23 (4.07)	1290	1220	975	−17.01
3d ($C_{27}H_{19}O_4SP$)	209–10	76	68.83 (68.93)	4.15 (4.07)	1310	1210	985	−17.04
3e ($C_{28}H_{21}O_4SP$)	212–13	85	69.54 (69.41)	4.42 (4.37)	1300	1220	970	−17.09
3f ($C_{28}H_{21}O_4SP$)	243–44	77	69.36 (69.41)	4.39 (4.37)	1310	1210	950	−17.15
3g ($C_{28}H_{21}O_4SP$)	224–25	78	69.29 (69.41)	4.26 (4.37)	1290	1220	960	−17.21
3h ($C_{27}H_{18}ClO_4SP$)	217–18	72	64.17 (64.23)	3.62 (3.59)	1290	1200	960	−17.02
3i ($C_{26}H_{16}ClO_4SP$)	198–99	71	63.68 (63.62)	3.37 (3.29)	1310	1210	975	−17.30
3j ($C_{26}H_{17}O_3SP$)	194–95	75	70.82 (70.90)	3.77 (3.89)	1310	1220	950	+12.41
3k ($C_{26}H_{23}O_3SP$)	215–16	72	69.83 (69.94)	5.26 (5.19)	1300	1235	965	+28.05
3l ($C_{24}H_{20}O_3NSP$)	250–51	71	66.52 (66.50)	4.78 (4.65)	1310	1220	970	—
3m ($C_{25}H_{22}O_3NSP$)	231–32	74	66.94 (67.10)	5.14 (4.96)	1290	1210	960	—
3n ($C_{24}H_{20}O_4NSP$)	189–90	75	63.98 (64.14)	4.54 (4.49)	1310	1200	980	—

[a] Recrystallized from isopropanol.
[b] ^{31}P chemical shifts were expressed in δ, from 85% H_3PO_4 as external standard.

the condensation of **1** with phosphorus oxychloride in the presence of triethylamine in dry toluene at 40–50°C. This intermediate, on subsequent reaction with cyclic amines, **5l–5n**, in situ, afforded the corresponding products (**3l–3n**). Physical properties, characteristic IR frequencies [3], and ^{31}P NMR data are shown in Table 1.

The ^{1}H NMR spectra (Table 2) exhibited only six signals in the region δ 7.30–8.98 for 12 protons of dinaphthodioxathiaphosphocin moieties [4]. This

TABLE 2 ^1H Chemical Shifts (δ) of 8-Substituted Dinaphtho[2, 1-d: 1′, 2′-g][1, 3, 6, 2] dioxathiaphosphocin 8-Oxides (**3**)[a,b]

Compound	*H(1/15)*	*H(2/14)*	*H(3/13)*	*H(4/12)*	*H(5/11)*	*H(6/10)*	*R–H*
3a	8.82 (8.3)	7.64 (7.4, 7.0)	7.48 (7.4, 7.1)	7.78 (7.8)	7.80 (7.4)	7.32 (7.6)	7.23–7.42 (m, 5H, Ar–H)
3b	8.82 (8.3)	7.63 (8.6, 7.1)	7.46 (7.6, 7.3)	7.78 (8.7)	7.80 (7.5)	7.30 (7.8)	7.07–7.29 (m, 4H, Ar–H) 2.43 (s, 3H, CH_3)
3c	8.82 (8.3)	7.62 (8.2, 7.0)	7.49 (7.4, 7.0)	7.78 (8.4)	7.80 (7.4)	7.30 (7.4)	7.04–7.19 (m, 4H, Ar–H) 2.40 (s, 3H, CH_3)
3d	8.83 (8.9)	7.62 (7.1, 6.8)	7.49 (7.3, 7.0)	7.79 (9.2)	7.81 (7.7)	7.30 (7.4)	7.13–7.25 (m, 4H, Ar–H) 2.38 (s, 3H, CH_3)
3e	8.82 (8.3)	7.60 (7.1, 7.0)	7.45 (8.0, 7.1)	7.76 (8.8)	7.77 (8.0)	7.32 (7.6)	7.07–7.10 (m, 3H, Ar–H) 2.30 (s, 3H, CH_3); 2.27 (s, 3H, CH_3)
3f	8.84 (8.8)	7.64 (7.2, 7.1)	7.49 (8.0, 7.1)	7.78 (7.7)	7.80 (7.0)	7.34 (7.4)	7.05–7.12 (m, 3H, Ar–H) 2.49 (s, 6H, CH_3)
3g	8.84 (8.6)	7.64 (7.2, 7.0)	7.48 (8.0, 7.2)	7.78 (7.4)	7.80 (8.2)	7.36 (7.7)	7.10–7.20 (m, 3H, Ar–H) 2.23 (s, 6H, CH_3)
3h	8.83 (8.3)	7.64 (8.2, 7.0)	7.50 (7.2, 7.0)	7.78 (7.8)	7.82 (8.4)	7.39 (7.5)	7.11–7.42 (m, 3H, Ar–H) 2.39 (s, 3H, CH_3)
3i	8.83 (8.3)	7.62 (7.1, 6.9)	7.49 (7.8, 7.2)	7.79 (8.8)	7.81 (8.3)	7.42 (7.4)	7.12–7.30 (m, 4H, Ar–H)
3j	8.86 (8.7)	7.78 (8.6, 7.1)	7.58 (7.8, 6.8)	8.03 (7.9)	8.08 (8.4)	7.48 (8.8)	7.70–8.16 (m, 5H, Ar–H)
3k	8.81 (8.7)	7.75 (7.7, 7.4)	7.58 (7.7, 7.3)	8.01 (7.8)	8.08 (9.1)	7.48 (8.8)	1.34–2.23 [m, 11H, $CH(CH_2)_5$]
3l	8.96 (8.3)	7.74 (8.2, 7.3)	7.51 (7.8, 7.3)	7.93 (7.9)	7.99 (8.8)	7.42 (8.8)	3.00–3.18 (m, 4H, 2′, 5′–CH_2) 1.14–1.20 (m, 4H, 3′, 4′–CH_2)
3m	8.97 (8.4)	7.78 (8.3, 7.2)	7.52 (7.9, 7.3)	7.92 (8.0)	7.98 (8.7)	7.40 (8.8)	3.52–3.62 (m, 4H, 2′, 6′–CH_2) 1.22–1.66 (m, 6H, 3′, 4′, 5′–CH_2)
3n	8.98 (8.8)	7.73 (8.3, 7.1)	7.52 (7.7, 7.3)	7.94 (8.2)	7.98 (9.1)	7.38 (8.8)	3.74–3.76 (m, 4H, 3′, 5′–CH_2) 3.34–3.60 (m, 4H, 2′, 6′–CH_2)

[a] *Recorded in* $DCCl_3$.

[b] Values in parentheses are coupling constants, J in Hz.

suggested a symmetrical arrangement of the two naphthyl units around the central dioxathiaphosphocin ring. The aromatic and aliphatic protons of 8-substituted moieties showed signals in the regions δ 7.04–8.16 and δ 1.15–3.76, respectively [5].

In the ^{13}C NMR spectra (Table 3), also only 10 signals appeared for the 20 carbon atoms of the dinaphthodioxathiaphosphocin moieties, which also confirms the symmetrical disposition of the naphthyl groups [4]. The ^{13}C chemical shifts were in-

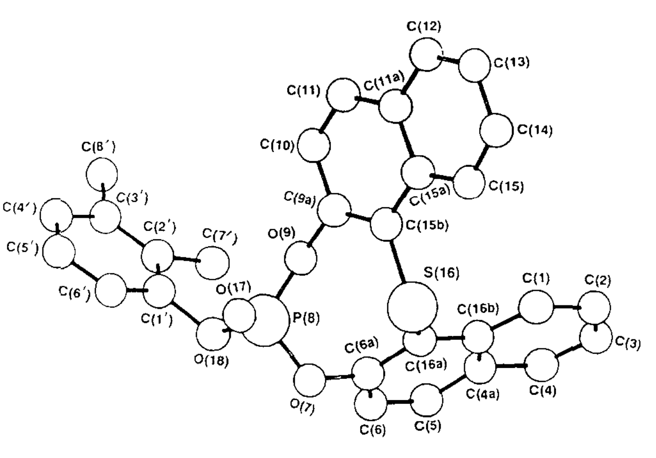


FIGURE 1 The molecular diagram and the atom-numbering scheme.

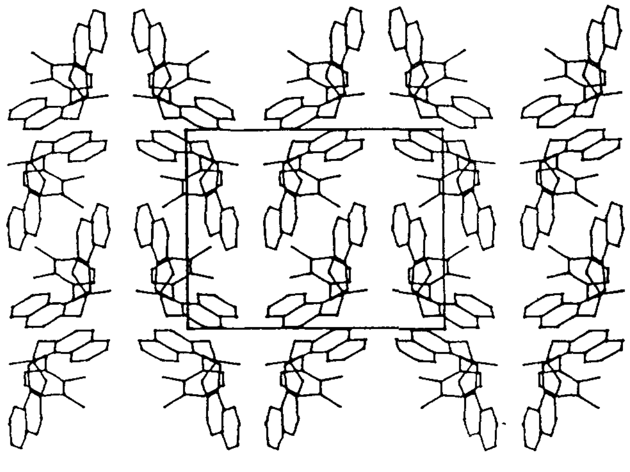


FIGURE 2 Packing of the molecules viewed down the "*C*" axis.

TABLE 3 ^{13}C Chemical Shifts (δ) of 8-Substituted Dinaphtho[2, 1-d: 1′, 2′-g][1, 3, 6, 2] dioxathiaphosphocin 8-Oxides (**3**)[a,b]

Carbons	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3j**	**3k**	**3l**	**3n**
C(1,15)	128.5	128.4	128.4	128.4	128.4	128.4	128.4	128.5	128.5	128.7	128.6	128.4	128.5
C(2,14)	128.1	128.0	128.0	127.9	127.9	128.0	127.9	128.1	128.0	128.3	128.3	127.8	127.8
C(3,13)	125.7	125.7	125.7	125.7	125.6	125.7	125.7	125.7	125.7	125.0	125.0	125.2	125.2
C(4,12)	131.4	131.4	131.4	131.4	131.4	131.4	131.4	131.5	131.4	131.4	131.3	131.5	131.2
C(5,11)	126.1	126.1	126.0	125.9	125.9	125.9	126.0	126.1	126.1	126.1	126.0	125.7	125.6
C(6,10)	119.9	119.9	119.9	120.0	119.9	119.9	120.0	119.9	119.9	120.8	120.5	122.2	122.4
	(6.0)	(6.0)	(6.0)	(6.3)	(5.9)	(5.9)	(5.8)	(6.1)	(6.0)	(4.9)		(3.8)	(3.3)
C(6a,9a)	152.5	152.5	152.6	152.5	151.7	152.6	152.6	152.4	152.5	152.1	152.5	152.8	153.2
	(9.3)	(9.4)	(9.4)	(9.3)	(9.4)	(9.4)	(9.4)	(9.4)	(9.3)	(11.3)	(9.7)	(9.5)	
C(15b,16a)	119.4	119.4	119.4	119.4	119.4	119.4	119.5	119.4	119.4	119.4	119.0	120.5	120.7
	(4.9)	(5.0)	(4.9)	(5.0)	(4.9)	(5.0)		(4.9)	(4.9)	(4.6)	(5.1)	(5.3)	(5.3)
C(4a,11a)	131.9	131.9	131.9	131.9	131.9	131.9	131.9	132.0	131.9	131.9	131.8	131.2	131.4
C(15a,16b)	134.8	134.8	134.8	134.8	134.8	134.9	134.8	134.8	134.8	134.2	134.3	134.5	134.6
								(1.6)	(1.7)			(1.2)	
C(1′)	150.4	149.1	150.2	148.3	149.1	148.5	148.2	147.6	146.6	131.4	35.6	—	—
	(7.9)	(8.3)		(8.0)	(8.3)	(9.4)		(7.9)		(7.4)	(141.9)		
C(2′)	120.5	129.9	120.9	120.2	128.3	130.4	121.3	130.7	130.8	131.0	25.7	44.8	44.2
	(4.3)		(4.9)	(4.6)		(4.8)	(4.9)	(4.8)		(10.5)	(4.9)	(4.5)	
C(3′)	129.9	131.6	140.2	130.3	139.1	129.1	138.4	131.5	128.1	129.3	25.9	23.5	65.9
											(17.2)	(11.2)	(4.7)
C(4′)	125.7	127.2	126.5	135.4	126.1	125.6	134.0	131.2	126.5	133.5	26.9	23.5	—
												(11.2)	—
C(5′)	129.9	127.2	129.5	130.3	127.1	129.1	130.6	127.0	125.7	129.3	25.90	44.8	65.9
											(17.2)	(4.3)	(4.7)
C(6′)	120.5	120.2	117.3	120.2	117.7	130.4	117.4	121.3	121.8	131.0	25.7	—	44.2
	(4.3)	(2.4)	(4.8)		(2.4)		(4.7)	(2.3)	(2.6)	(10.5)	(4.9)		
Methyl Carbons	—	16.2	21.3	20.7	12.6, 20.2	17.3	19.9, 19.1	16.4	—	—	—	—	—

[a] Values in parentheses are coupling constants J_{PC} in Hz.
[b] Recorded in $DCCl_3$.

TABLE 4 Mass Spectral Data (% of Important Ions) of Certain Members of **3**

		$(M-R)^+$	$[(M-R)-PO_2]^+$	$[(M-RPO_2)-S]^+$	$[(M-R)-C_{10}H_6O)]^+$	$[(M-R)-C_{10}H_6S]^+$	$[(M-R)-C_{10}H_6OS]^+$
Compound	M^+(%)	*363*	*300*	*268*	*221*	*205*	*189*
3a	456 (63.4)	100	20.4	14.9	2.9	59.3	7.1
3b	470 (44.9)	100	2.5	7.5	1.3	27.5	0.6
3c	470 (47.6)	100	10.9	14.6	2.5	52.4	9.7
3d	470 (47.8)	100	25.4	21.3	2.6	55.2	4.6
3e	484 (77.8)	100	11.1	8.8	11.0	77.8	11.2
3f	484 (18.3)	100	11.6	8.3	1.3	31.6	1.7
3g	484 (37.4)	100	14.6	13.4	6.2	47.6	4.9
3h	504 (20.0)	100	16.7	10.0	1.4	36.7	5.9
3i	490 (48.8)	100	14.3	11.6	1.8	51.2	6.9
3j	440 (100)	—	4.8	—	—	37.2	11.9
3k	445 (88.2)	16.2	11.2	10.8	0.9	100.0	28.5
3n	449 (14.3)	17.7	12.2	21.4	9.5	45.2	52.4

TABLE 5 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3e**

	x	*y*	*z*	*U*(*eq*)[a]
P(8)	8330(1)	6073(1)	3154(1)	63(1)
S(16)	8131(1)	6257(1)	558(1)	62(1)
O(17)	8154(2)	7009(1)	3184(2)	74(1)
O(7)	7340(2)	5504(1)	2454(2)	59(1)
O(9)	9382(2)	5796(2)	2781(2)	80(1)
O(18)	8599(2)	5570(2)	4260(2)	78(1)
C(6a)	6512(2)	5795(2)	1559(2)	53(1)
C(6)	5423(3)	5695(2)	1634(3)	67(1)
C(5)	4561(3)	5943(2)	806(3)	77(1)
C(4a)	4733(2)	6301(2)	−141(3)	66(1)
C(4)	3833(3)	6569(3)	−1006(4)	85(1)
C(3)	4007(4)	6914(3)	−1905(4)	96(1)
C(2)	5099(4)	7014(2)	−1996(3)	86(1)
C(1)	5994(3)	6755(2)	−1186(3)	69(1)
C(16b)	5840(2)	6388(2)	−231(2)	54(1)
C(16a)	6739(2)	6110(2)	644(2)	50(1)
C(15b)	8778(2)	5228(2)	982(2)	53(1)
C(15a)	8809(2)	4543(2)	243(3)	53(1)
C(15)	8314(2)	4614(2)	−872(3)	65(1)
C(14)	8381(3)	3940(3)	−1553(3)	81(1)
C(13)	8945(3)	3162(3)	−1146(4)	89(1)
C(12)	9435(3)	3072(2)	−92(4)	80(1)
C(11a)	9397(2)	3755(2)	645(3)	63(1)
C(11)	9943(3)	3684(2)	1744(3)	78(1)
C(10)	9928(3)	4350(3)	2431(3)	78(1)
C(9a)	9346(2)	5115(2)	2042(3)	65(1)
C(1′)	7852(3)	5598(2)	4925(2)	68(1)
C(2′)	7327(3)	4822(2)	5078(3)	76(1)
C(3′)	6643(4)	4856(2)	5767(3)	83(1)
C(4′)	6549(4)	5621(3)	6293(3)	100(1)
C(5′)	7094(4)	6374(3)	6135(3)	96(1)
C(6′)	7749(3)	6370(2)	5443(3)	74(1)
C(7′)	7540(5)	3994(3)	4523(4)	121(2)
C(8′)	5999(6)	4044(3)	5935(5)	135(2)

[a] *U*(*eq*) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 6 Bond Lengths (Å) for Nonhydrogen Atoms of **3e**

P(8)–O(17)	1.441(2)	C(16b)–C(16a)	1.423(4)[a]
P(8)–O(9)	1.572(2)	C(15b)–C(9a)	1.370(4)
P(8)–O(18)	1.575(3)	C(15b)–C(15a)	1.420(4)
P(8)–O(7)	1.576(2)	C(15a)–C(15)	1.409(4)
S(16)–C(15b)	1.777(3)	C(15a)–C(11a)	1.426(4)
S(16)–C(16a)	1.782(3)	C(15)–C(14)	1.368(5)
O(7)–C(6a)	1.396(4)	C(14)–C(13)	1.402(6)
O(9)–C(9a)	1.401(4)	C(13)–C(12)	1.340(6)
O(18)–C(1′)	1.429(4)	C(12)–C(11a)	1.418(5)
C(6a)–C(16a)	1.374(4)	C(11a)–C(11)	1.402(5)
C(6a)–C(6)	1.395(4)	C(11)–C(10)	1.350(5)
C(6)–C(5)	1.349(5)	C(10)–C(9a)	1.391(5)
C(5)–C(4a)	1.407(5)	C(1′)–C(6′)	1.374(5)
C(4a)–C(4)	1.412(5)	C(1′)–C(2′)	1.388(5)
C(4a)–C(16b)	1.422(4)	C(2′)–C(3′)	1.390(5)
C(4)–C(3)	1.345(6)	C(2′)–C(7′)	1.507(5)
C(3)–C(2)	1.406(6)	C(3′)–C(4′)	1.369(5)
C(2)–C(1)	1.364(5)	C(3′)–C(8′)	1.519(6)
C(1)–C(16b)	1.413(5)	C(4′)–C(5′)	1.374(6)
C(5′)–C(6′)	1.365(6)		

[a] esd's in parentheses.

terpreted based on the comparison with carbon chemical shifts of **1** and related systems [4–7]. Six dinaphthyl carbons 6, 6a, 9a, 10, 15b, and 16a experienced coupling with phosphorus. The oxygen bearing-carbons C(6a) and C(9a), resonated, in the region δ 151.7–152.8 as a doublet [$^2J_{POC(6a,9a)}$ = 9.3–11.3 Hz]. The doublet at δ 119.9–122.4 with the $^3J_{POCC}$ = 3.3–6.3 Hz for each compound **3** was assigned to C(6,10). Chemical shifts at δ 119.0–120.7 with the $^3J_{POCC}$ = 4.6–5.3 Hz were ascribed to C(15b,16a). Low-intensity signals in the regions δ 131.2–132.0 and δ 134.2–134.9 were attributed to the tertiary carbons C(4a,11a) and C(15a,16b). Signals for C(1,15), C(2,14), C(3,13), C(4,12), and C(5,11) occurred in the regions δ 128.4–128.7, 127.8–128.3, 125.0–125.7, 131.2–131.5, and 125.6–126.1, respectively [4]. The carbons of 8-substituted moieties showed substantial variation in their chemical shifts [4–9]. The doublets at δ 146.6–150.4 [$^2J_{POC(1')}$ = 7.4–9.4 Hz] were ascribed to C(1′) of **3a–3i**. An upfield shift of about 5 ppm for the methyl group attached to C(2′) in **3b** and **3h** is due to its γ interaction with exocyclic oxygen [4,6,9]. More shielding of C(2′) by 8 ppm in **3e** is the result of double γ interaction both with exocyclic oxygen and the C(3′) methyl group [4,9]. In **3j**, C(1′) and C(2′) absorbed at δ 131.4 [$J_{PC(1')}$ = 7.4 Hz] and 131.0 [$^2J_{PCC(2')}$ = 4.9 Hz], respectively [4]. The carbons C(1′), C(2′), and C(3′) in **3k** showed couplings with phosphorus at δ 35.6 [$J_{PC(1')}$ = 141.9 Hz], 25.7 [$^2J_{PCC(2')}$ = 4.9 Hz], and 25.9 [$^3J_{PCCC(3')}$ = 17.2 Hz], respectively. The carbons C(2′,5′) and C(3′,4′) in **3l** coupled to phosphorus at δ 44.8 [$^2J_{PNC(2',5')}$ = 4.3 Hz] and 23.5 [$^3J_{PNCC(3',4')}$ = 11.2 Hz], while C(3′,5′) in **3n** resolved as a doublet at δ 65.9 [$^3J_{PNCC(3',5')}$ = 4.7 Hz] [5a].

The ^{31}P NMR signals (Table 1) for the 8-aryloxy compounds **3a–3i** occurred at δ − 17.01 to − 17.30 [4,5b]. For the 8-aryl and 8-alkyl derivatives, **3j** and **3k**, the signals appeared at δ +12.41 and +28.05, respectively [5b].

Electron impact mass spectra (Table 4) exhibited M^+ and $(M\text{–}R)^+$. $(M\text{–}R)^+$ due to dinaphtho[2,1-d:1′,2′-g][1,3,6,2]dioxathiaphosphocin 8-oxide ion appeared as the base peak in 8-aryloxy compounds (**3a–3i**). Other characteristic daughter ions are $[(M\text{–}R)\text{–}PO_2]^+$, $[(M\text{–}RPO_2)\text{–}S]^+$, $[(M\text{–}R)\text{–}C_{10}H_6O]^+$, $[(M\text{–}R)\text{–}C_{10}H_6S]^+$, and $[(M\text{–}R)\text{–}C_{10}H_6OS]$ at *m*/*z* 300, 268, 221, 205, and 189, respectively.

The structure of a crystal of **3e** was determined by X-ray diffraction analysis in an effort to establish the overall geometry of the system and to confirm its identity. The final positional and equivalent isotropic temperature factors of the nonhydrogen atoms are given in Table 5. The perspective view of the molecule and the atom-num-

TABLE 7 Bond Angles (°) for **3e**

O(17)–P(8)–O(9)	114.7(2)	C(9a)–C(15b)–S(16)	119.1(2)[a]
O(17)–P(8)–O(18)	116.82(14)	C(15a)–C(15b)–S(16)	122.0(2)
O(9)–P(8)–O(18)	99.07(14)	C(15)–C(15a)–C(15b)	123.2(3)
O(17)–P(8)–O(7)	117.12(13)	C(15)–C(15a)–C(11a)	118.4(3)
O(9)–P(8)–O(7)	105.40(12)	C(15b)–C(15a)–C(11a)	118.4(3)
O(18)–P(8)–O(7)	101.26(13)	C(14)–C(15)–C(15a)	120.9(3)
C(15b)–S(16)–C(16a)	103.75(12)	C(15)–C(14)–C(13)	120.1(4)
C(6a)–O(7)–P(8)	126.1(2)	C(12)–C(13)–C(14)	120.8(4)
C(9a)–O(9)–P(8)	122.1(2)	C(13)–C(12)–C(11a)	121.2(4)
C(1′)–O(18)–P(8)	121.2(2)	C(11)–C(11a)–C(12)	121.8(3)
C(16a)–C(6a)–O(7)	123.0(2)	C(11)–C(11a)–C(15a)	119.6(3)
C(16a)–C(6a)–C(6)	122.0(3)	C(12)–C(11a)–C(15a)	118.5(3)
O(7)–C(6a)–C(6)	114.9(3)	C(10)–C(11)–C(11a)	121.2(3)
C(5)–C(6)–C(6a)	119.6(3)	C(11)–C(10)–C(9a)	119.2(4)
C(6)–C(5)–C(4a)	121.4(3)	C(15b)–C(9a)–O(9)	120.1(3)
C(4)–C(4a)–C(5)	121.6(3)	C(15b)–C(9a)–C(10)	122.9(3)
C(4)–C(4a)–C(16b)	119.2(4)	O(9)–C(9a)–C(10)	117.0(3)
C(5)–C(4a)–C(16b)	119.2(3)	C(6′)–C(1′)–C(2′)	123.1(4)
C(3)–C(4)–C(4a)	121.1(4)	C(6′)–C(1′)–O(18)	118.7(3)
C(4)–C(3)–C(2)	120.1(4)	C(2′)–C(1′)–O(18)	118.0(3)
C(1)–C(2)–C(3)	120.9(4)	C(1′)–C(2′)–C(3′)	117.0(3)
C(2)–C(1)–C(16b)	120.5(4)	C(1′)–C(2′)–C(7′)	119.4(4)
C(1)–C(16b)–C(4a)	118.2(3)	C(3′)–C(2′)–C(7′)	123.5(4)
C(1)–C(16b)–C(16a)	123.2(3)	C(4′)–C(3′)–C(2′)	119.9(4)
C(4a)–C(16b)–C(16a)	118.6(3)	C(4′)–C(3′)–C(8′)	119.9(4)
C(6a)–C(16a)–C(16b)	119.1(2)	C(2′)–C(3′)–C(8′)	120.1(4)
C(6a)–C(16a)–S(16)	121.9(2)	C(3′)–C(4′)–C(5′)	121.4(4)
C(16b)–C(16a)–S(16)	118.8(2)	C(6′)–C(5′)–C(4′)	120.1(4)
C(9a)–C(15b)–C(15a)	118.6(3)	C(1′)–C(6′)–C(5′)	118.3(4)

[a] esd's in parentheses.

bering scheme are shown in Figure 1. The bond lengths and bond angles are given in Tables 6 and 7, respectively.

In the dioxathiaphosphocin ring system, the endo- and exocyclic P–O distances P(8)–O(7) [1.576 Å], P(8)–O(9) [1.572 Å], P(8)–O(18) [1.575 Å] are comparable with the value of (1.581 Å) reported for the dinaphthodioxaphosphocin ring [4]. The P=O bond length [1.441 Å] agrees with the value of (1.45 Å) found in the dibenzodithiaphosphepin ring [10] and is slightly shorter than those of other dinaphthodioxaphosphocin rings [4,11]. The mean C–S bond distance (1.779 Å) is slightly different from the value of (1.784 Å) obtained in the eight-membered dioxathiaphosphocin ring [12]. The endocyclic angle O(7)–P(8)–O(9) [105.4°] at phosphorus is comparable with that of eight-membered cyclic organophosphorus compounds [4,11,13,14].

The mean plane passing through the heterocyclic ring showed that P(8), C(16a), S(16), and O(9) are above and O(7), C(6a), C(15b), and C(9a) are below the plane. The torsion angles of the heterocyclic ring (Table 8) provide additional evidence that the ring is not planar, but puckered. This ring assumed a distorted-boat–like conformation due to its fusion to the bulky naphthyl groups. This structure is stabilized by van der Waals forces. Packing of the molecules in the unit cell viewed down the 'c' axis is shown in Figure 2. Least-square planes and deviations, hydrogen coordinates and isotropic displacement parameters, bond lengths and bond angles for hydrogen atoms, crystal data and structure refinement, and anisotropic displacement parameters for nonhydrogen atoms are given in Tables 9, 10, 11, 12 and 13, respectively.

EXPERIMENTAL

Melting points are uncorrected. Microanalyses and electron impact mass spectra were recorded by RSIC, Central Drug Research Institute, Lucknow, India. IR spectra were recorded as KBr pellets on a Perkin-Elmer 683 unit. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-300 MHz spectrometer operating at 300, 75, and 121 MHz, respectively, in DCCl$_3$ solutions and were referenced from TMS (^{1}H and ^{13}C) or 85% H$_3$PO$_4$ (^{31}P).

8-(Phenoxy)dinaphtho[2,1-d:1′,2′-g][1,3,6,2]dioxathiaphosphocin 8-Oxide (**3a**)

Phenyl phosphorodichloridate (**2a**, 2.1 g, 0.01 mol) in dry toluene (30 mL) was added dropwise over a

TABLE 8 Torsion Angles (°) for **3e**

O(17)–P(8)–O(7)–C(6a)	26.78 (0.26)[a]
O(9)–P(8)–O(7)–C(6a)	−102.19 (0.23)
O(18)–P(8)–O(7)–C(6a)	155.01 (0.21)
O(17)–P(8)–O(9)–C(9a)	−135.47 (0.26)
O(18)–P(8)–O(9)–C(9a)	99.32 (0.27)
O(7)–P(8)–O(9)–C(9a)	−5.11 (0.29)
O(17)–P(8)–O(18)–C(1′)	57.64 (0.28)
O(9)–P(8)–O(18)–C(1′)	−178.61 (0.23)
O(7)–P(8)–O(18)–C(1′)	−70.79 (0.25)
P(8)–O(7)–C(6a)–C(16a)	60.80 (0.34)
P(8)–O(7)–C(6a)–C(6)	−122.76 (0.24)
C(16a)–C(6a)–C(6)–C(5)	−2.59 (0.46)
O(7)–C(6a)–C(6)–C(5)	−179.06 (0.27)
C(6a)–C(6)–C(5)–C(4a)	0.22 (0.49)
C(6)–C(5)–C(4a)–C(4)	−179.47 (0.31)
C(6)–C(5)–C(4a)–C(16b)	1.04 (0.47)
C(5)–C(4a)–C(4)–C(3)	179.68 (0.34)
C(16b)–C(4a)–C(4)–C(3)	−0.83 (0.50)
C(4a)–C(4)–C(3)–C(2)	−0.07 (0.57)
C(4)–C(3)–C(2)–C(1)	0.89 (0.57)
C(3)–C(2)–C(1)–C(16b)	−0.79 (0.51)
C(2)–C(1)–C(16b)–C(4a)	−0.12 (0.43)
C(2)–C(1)–C(16b)–C(16a)	−179.64 (0.28)
C(4)–C(4a)–C(16b)–C(1)	0.91 (0.41)
C(5)–C(4a)–C(16b)–C(1)	−179.59 (0.28)
C(4)–C(4a)–C(16b)–C(16a)	−179.55 (0.26)
C(5)–C(4a)–C(16b)–C(16a)	−0.04 (0.41)
O(7)–C(6a)–C(16a)–C(16b)	179.74 (0.23)
C(6)–C(6a)–C(16a)–C(16b)	3.55 (0.40)
O(7)–C(6a)–C(16a)–S(16)	−5.04 (0.37)
C(6)–C(6a)–C(16a)–S(16)	178.77 (0.22)
C(1)–C(16b)–C(16a)–C(6a)	177.34 (0.26)
C(4a)–C(16b)–C(16a)–C(6a)	−2.18 (0.38)
C(1)–C(16b)–C(16a)–S(16)	1.97 (0.36)
C(4a)–C(16b)–C(16a)–S(16)	−177.55 (0.20)
C(15b)–S(16)–C(16a)–C(6a)	51.26 (0.26)
C(15b)–S(16)–C(16a)–C(16b)	−133.51 (0.22)
C(16a)–S(16)–C(15b)–C(9a)	−93.65 (0.24)
C(16a)–S(16)–C(15b)–C(15a)	91.97 (0.22)
C(9a)–C(15b)–C(15a)–C(15)	−175.90 (0.25)
S(16)–C(15b)–C(15a)–C(15)	−1.49 (0.35)
C(9a)–C(15b)–C(15a)–C(11a)	2.27 (0.36)
S(16)–C(15b)–C(15a)–C(11a)	176.68 (0.19)
C(15b)–C(15a)–C(15)–C(14)	179.00 (0.27)
C(11a)–C(15a)–C(15)–C(14)	0.83 (0.40)
C(15a)–C(15)–C(14)–C(13)	0.28 (0.47)
C(15)–C(14)–C(13)–C(12)	−0.83 (0.52)
C(14)–C(13)–C(12)–C(11a)	0.22 (0.53)
C(13)–C(12)–C(11a)–C(11)	−177.44 (0.32)
C(13)–C(12)–C(11a)–C(15a)	0.90 (0.46)
C(15)–C(15a)–C(11a)–C(11)	176.97 (0.27)
C(15b)–C(15a)–C(11a)–C(11)	−1.29 (0.38)
C(15)–C(15a)–C(11a)–C(12)	−1.40 (0.38)
C(15b)–C(15a)–C(11a)–C(12)	−179.66 (0.25)
C(12)–C(11a)–C(11)–C(10)	178.03 (0.33)
C(15a)–C(11a)–C(11)–C(10)	−0.28 (0.49)
C(11a)–C(11)–C(10)–C(9a)	0.84 (0.54)
C(15a)–C(15b)–C(9a)–O(9)	176.60 (0.23)
S(16)–C(15b)–C(9a)–O(9)	2.03 (0.36)
C(15a)–C(15b)–C(9a)–C(10)	−1.80 (0.43)
S(16)–C(15b)–C(9a)–C(10)	−176.37 (0.25)
P(8)–O(9)–C(9a)–C(15b)	70.75 (0.36)
P(8)–O(9)–C(9a)–C(10)	−110.76 (0.30)
C(11)–C(10)–C(9a)–C(15b)	0.22 (0.52)
C(11)–C(10)–C(9a)–O(9)	−178.22 (0.31)
P(8)–O(18)–C(1′)–C(6′)	−70.76 (0.35)
P(8)–O(18)–C(1′)–C(2′)	113.90 (0.29)
C(6′)–C(1′)–C(2′)–C(3′)	2.02 (0.52)
O(18)–C(1′)–C(2′)–C(3′)	177.14 (0.30)
C(6′)–C(1′)–C(2′)–C(7′)	−176.55 (0.36)
O(18)–C(1′)–C(2′)–C(7′)	−1.43 (0.48)
C(1′)–C(2′)–C(3′)–C(4′)	−2.65 (0.56)
C(7′)–C(2′)–C(3′)–C(4′)	175.85 (0.40)
C(1′)–C(2′)–C(3′)–C(8′)	177.17 (0.38)
C(7′)–C(2′)–C(3′)–C(8′)	−4.33 (0.63)
C(2′)–C(3′)–C(4′)–C(5′)	1.75 (0.68)
C(8′)–C(3′)–C(4′)–C(5′)	−178.07 (0.45)
C(3′)–C(4′)–C(5′)–C(6′)	−0.04 (0.71)
C(2′)–C(1′)–C(6′)–C(5′)	−0.38 (0.54)
O(18)–C(1′)–C(6′)–C(5′)	−175.46 (0.32)
C(4′)–C(5′)–C(6′)–C(1′)	−0.65 (0.61)

[a] esd's in parentheses.

period of 20 minutes to a stirred solution of bis(2-hydroxy-1-naphthyl)sulfide (**1**, 3.18 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in dry toluene (70 mL) at room temperature. After completion of the addition, the reaction mixture was slowly heated to 55–65°C and was maintained at this temperature for 6 hours. TLC was used to monitor the progress of the reaction. Separation of triethylamine hydrochloride by filtration afforded a filtrate that was evaporated under reduced pressure to give a solid residue. The crude product was washed with water and recrystallized from 2-propanol, yield 60%, mp 186–87°C. The other compounds **3b–3k** were also prepared in the same fashion.

8-(1-Morpholinyl)dinaphtho [2,1-d:1′,2′-g][1,3,6,2]dioxathiaphosphocin 8-Oxide (**3n**)

A solution of phosphorus oxychloride (1.53 g, 0.01 mol) in dry, toluene (30 mL) was added dropwise to a stirred solution of bis(2-hydroxy-1-naphthyl)sulfide (**1**, 3.18 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in dry toluene (70 mL) at 0–5°C. After having been stirred for 4 hours at 40–50°C, the reaction mixture by TLC analysis indicated the formation of the 8-chloro-dinaphtho[2,1-d:1′,2′-g][1,3,6,2]dioxathiaphosphocin 8-oxide (**4**). The reaction mixture was cooled to 10–20°C, and a solution of morpholine (**5n**, 0.87 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in toluene (20 mL)

TABLE 9 Least-Squares Planes (x, y, z in Crystal Coordinates) and Deviations from Them of **3e**

Plane 1

2.837 (0.012) x + 14.763 (0.008) y + 0.049 (0.011) z = 10.764 (0.009)
*[a] 0.580 (0.002) P(8)
* −0.544 (0.002) O(7)
* −0.354 (0.002) C(6a)
* 0.171 (0.002) C(16a)
* 0.783 (0.002) S(16)
* −0.551 (0.002) C(15b)
* −0.551 (0.002) C(9a)
* 0.468 (0.002) O(9)
Rms deviation of fitted atoms = 0.528

Plane 2

8.909 (0.008) x − 3.095 (0.027) y + 5.812 (0.010) z = 7.928 (0.019)
Angle to previous plane (with approximate esd) = 89.40 (0.12)
* −0.554 (0.002) P(8)
* 0.485 (0.002) O(18)
* 0.197 (0.003) C(1′)
* 0.058 (0.003) C(2′)
* −0.161 (0.003) C(3′)
* −0.177 (0.004) C(4′)
* −0.015 (0.003) C(5′)
* 0.167 (0.003) C(6′)
Rms deviation of fitted atoms = 0.289

Plane 3

11.341 (0.008) x + 5.894 (0.012) y − 5.006 (0.008) z = 12.574 (0.007)
Angle to previous plane (with approximate esd) = 61.71 (0.07)
* −0.029 (0.002) C(15b)
* −0.027 (0.002) C(15a)
* 0.011 (0.002) C(15)
* 0.031 (0.003) C(14)
* 0.008 (0.003) C(13)
* −0.017 (0.003) C(12)
* −0.026 (0.003) C(11a)
* 0.001 (0.003) C(11)
* 0.032 (0.003) C(10)
* 0.018 (0.002) C(9a)
Rms deviation of fitted atoms = 0.022

Plane 4

−0.752 (0.012) x + 13.941 (0.008) y + 5.107 (0.008) z = 8.360 (0.009)
Angle to previous plane (with approximate esd) = 75.92 (0.07)
* 0.024 (0.002) C(6a)
* 0.005 (0.003) C(6)
* −0.006 (0.003) C(5)
* −0.004 (0.003) C(4a)
* −0.005 (0.003) C(4)
* 0.004 (0.003) C(3)
* 0.015 (0.003) C(2)
* −0.001 (0.003) C(1)
* −0.012 (0.002) C(16b)
* −0.021 (0.002) C(16a)
Rms deviation of fitted atoms = 0.012

[a] Indicates atom used to define plane.

TABLE 10 Hydrogen Coordinates $(\times 10^4)$ and Isotropic Displacement Parameters (Å^2 × 10^3) of **3e**

	x	y	z	$U(eq)$
H(6)	5292(3)	5458(2)	2253(3)	81
H(5)	3836(3)	5877(2)	862(3)	92
H(4)	3107(3)	6506(3)	−954(4)	102
H(3)	3404(4)	7086(3)	−2468(4)	115
H(2)	5214(4)	7261(2)	−2616(3)	103
H(1)	6711(3)	6819(2)	−1263(3)	83
H(15)	7935(2)	5127(2)	−1149(3)	78
H(14)	8053(3)	3997(3)	−2287(3)	98
H(13)	8979(3)	2704(3)	−1613(4)	106
H(12)	9807(3)	2552(2)	161(4)	96
H(11)	10323(3)	3168(2)	2004(3)	93
H(10)	10301(3)	4297(3)	3157(3)	94
H(4′)	6105(4)	5633(3)	6767(3)	120
H(5′)	7017(4)	6887(3)	6501(3)	115
H(6′)	8116(3)	6878(2)	5324(3)	89
H(7′a)	6938(17)	3900(15)	3888(19)	182
H(7′b)	7590(35)	3503(5)	5001(13)	182
H(7′c)	8227(18)	4052(11)	4327(29)	182
H(8′a)	6430(17)	3527(4)	5900(36)	203
H(8′b)	5305(17)	4017(16)	5384(22)	203
H(8′c)	5854(33)	4076(15)	6627(16)	203

TABLE 11 Bond Lengths (Å) and Bond Angles (°) for Hydrogen Atoms of **3e**

C(6)–H(6)	0.93	C(10)–H(10)	0.93
C(5)–H(5)	0.93	C(4′)–H(4′)	0.93
C(4)–H(4)	0.93	C(5′)–H(5′)	0.93
C(3)–H(3)	0.93	C(6′)–H(6′)	0.93
C(2)–H(2)	0.93	C(7′)–H(7′a)	0.96
C(1)–H(1)	0.93	C(7′)–H(7′b)	0.96
C(15)–H(15)	0.93	C(7′)–H(7′c)	0.96
C(14)–H(14)	0.93	C(8′)–H(8′a)	0.96
C(13)–H(13)	0.93	C(8′)–H(8′b)	0.96
C(12)–H(12)	0.93	C(8′)–H(8′c)	0.96
C(11)–H(11)	0.93		
C(5)–C(6)–H(6)	120.2(2)	C(13)–C(12)–H(12)	119.4(2)
C(6a)–C(6)–H(6)	120.2(2)	C(11a)–C(12)–H(12)	119.4(2)
C(6)–C(5)–H(5)	119.3(2)	C(10)–C(11)–H(11)	119.4(2)
C(4a)–C(5)–H(5)	119.3(2)	C(11a)–C(11)–H(11)	119.4(2)
C(3)–C(4)–H(4)	119.4(2)	C(11)–C(10)–H(10)	120.4(2)
C(4a)–C(4)–H(4)	119.4(3)	C(9a)–C(10)–H(10)	120.4(2)
C(4)–C(3)–H(3)	120.0(2)	C(3′)–C(4′)–H(4′)	119.3(3)
C(2)–C(3)–H(3)	120.0(3)	C(5′)–C(4′)–H(4′)	119.3(3)
C(1)–C(2)–H(2)	119.6(3)	C(6′)–C(5′)–H(5′)	119.9(2)
C(3)–C(2)–H(2)	119.6(3)	C(4′)–C(5′)–H(5′)	119.9(3)
C(2)–C(1)–H(1)	119.8(3)	C(1′)–C(6′)–H(6′)	120.9(2)
C(16b)–C(1)–H(1)	119.8(2)	C(5′)–C(6′)–H(6′)	120.9(2)
C(14)–C(15)–H(15)	119.5(2)	C(2′)–C(7′)–H(7′a)	109.5(3)
C(15a)–C(15)–H(15)	119.5(2)	C(2′)–C(7′)–H(7′b)	109.5(2)
C(15)–C(14)–H(14)	119.9(2)	C(2′)–C(7′)–H(7′c)	109.5(3)
C(13)–C(14)–H(14)	119.9(2)	C(3′)–C(8′)–H(8′a)	109.5(3)
C(12)–C(13)–H(13)	119.6(2)	C(3′)–C(8′)–H(8′b)	109.5(3)
C(14)–C(13)–H(13)	119.6(2)	C(3′)–C(8′)–H(8′c)	109.5(3)

TABLE 12 Crystal Data and Structure Refinement of **3e**

Identification code	**3e**
Empirical formula	C_{28} H_{21} O_4 P S
Formula weight	484.4
Temperature	293 (2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.461(3) Å
	b = 15.198(6) Å
	c = 12.920(2) Å
	B = 105.74(2) Å
Volume	2355.1(11) $Å^3$
Z	4
Density (calculated)	1.366 g/cm^3
Absorption coefficient	0.239 mm^{-1}
$F(000)$	1008
Crystal size	0.5 × 0.4 × 0.3 mm
θ range for data collection	1.70–24.97°
Index ranges	$0 \le h \le 14$, $0 \le k \le 17$, $-15 \le l \le 14$
Reflections collected	3134
Independent reflections	2990 [R(int) = 0.0127]
Refinement method	Full-matrix least-squres on F^2
Data/restraints/parameters	2990/0/310
Goodness of fit on F^2	0.777
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0394, $wR2$ = 0.1295
R indices (all data)	$R1$ = 0.0419, $wR2$ = 0.1333
Extinction coefficient	0.0023(10)
Largest diffraction peak and hole	0.185 and −0.278 $e \cdot Å^{-3}$

TABLE 13 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3e**[a]

	U11	*U22*	*U33*	*U23*	*U13*	*U12*
P(8)	63(1)	57(1)	70(1)	−7(1)	17(1)	−2(1)
S(16)	43(1)	49(1)	103(1)	11(1)	32(1)	0(1)
O(17)	88(2)	54(1)	82(2)	−7(1)	24(1)	−7(1)
O(7)	57(1)	54(1)	70(1)	1(1)	23(1)	−4(1)
O(9)	55(1)	92(2)	92(2)	−24(1)	18(1)	−6(1)
O(18)	85(2)	71(2)	73(1)	−1(1)	14(1)	16(1)
C(6a)	46(2)	45(1)	72(2)	−9(1)	23(1)	−5(1)
C(6)	55(2)	66(2)	91(2)	−9(2)	37(2)	−12(1)
C(5)	42(2)	75(2)	120(3)	−20(2)	35(2)	−11(2)
C(4a)	45(2)	54(2)	94(2)	−20(2)	12(2)	0(1)
C(4)	53(2)	75(2)	115(3)	−30(2)	2(2)	6(2)
C(3)	79(3)	83(3)	100(3)	−30(2)	−21(2)	24(2)
C(2)	103(3)	70(2)	74(2)	−10(2)	4(2)	20(2)
C(1)	75(2)	56(2)	77(2)	−5(2)	21(2)	7(2)
C(16b)	47(2)	40(1)	73(2)	−12(1)	13(1)	2(1)
C(16a)	39(1)	40(1)	77(2)	−6(1)	24(1)	−4(1)
C(15b)	35(1)	54(2)	73(2)	6(1)	21(1)	1(1)
C(15a)	35(1)	55(2)	75(2)	4(1)	25(1)	−2(1)
C(15)	43(2)	77(2)	82(2)	3(2)	28(2)	−1(1)
C(14)	58(2)	106(3)	85(2)	−18(2)	28(2)	−10(2)
C(13)	73(2)	81(3)	123(4)	−35(3)	45(2)	−15(2)
C(12)	62(2)	62(2)	126(3)	−9(2)	45(2)	−2(2)
C(11a)	46(2)	54(2)	95(2)	1(2)	33(2)	−1(1)
C(11)	60(2)	67(2)	107(3)	21(2)	25(2)	17(2)
C(10)	61(2)	91(3)	78(2)	12(2)	11(2)	16(2)
C(9a)	43(2)	67(2)	85(2)	−6(2)	20(2)	0(1)
C(1′)	86(2)	56(2)	50(2)	1(1)	−2(2)	10(2)
C(2′)	112(3)	49(2)	51(2)	−3(1)	−5(2)	3(2)
C(3′)	117(3)	71(2)	59(2)	10(2)	19(2)	−7(2)
C(4′)	147(4)	83(3)	76(3)	7(2)	40(3)	13(3)
C(5′)	154(4)	61(2)	73(2)	−5(2)	31(3)	14(2)
C(6′)	107(3)	48(2)	62(2)	−2(2)	11(2)	2(2)
C(7′)	202(6)	61(2)	98(3)	−18(2)	34(3)	5(3)
C(8′)	183(6)	101(4)	121(4)	20(3)	38(4)	−39(4)

[a] The anisotropic displacement factor exponent takes the following form: $-2 \text{pi}^2 [h^2 ax^2\ U11 + \ldots + 2\ hka^*\ b^*\ U12]$.

was added dropwise. The resulting reaction mixture was stirred for 1 hour at room temperature and then for 2 hours at 50–60°C. Triethylamine hydrochloride was separated by filtration, and the solvent from the filtrate was removed under reduced pressure. The residue, after having been washed with water, was recrystallized from 2-propanol to give a white granular solid, yield 75%, mp 189–90°C. The compounds **3l** and **3m** were also prepared by the same procedure.

Crystal Structure Determination

A colorless single crystal of **3e** was obtained from methanol-toluene (2:1) by crystallization. A crystal measuring 0.5 × 0.4 × 0.3 mm was used for preliminary data collection, via the Weissenberg technique. Accurate cell dimensions were subsequently refined by the least-squares method using 25 medium-angle refractions ($25° < \theta < 35°$) collected with an Enraf-Nonius CAD-4 diffractometer.

The crystal data were $C_{28}H_{21}O_4SP$, $Mw = 484.4$, monoclinic, space group $P2_1/c$, $a = 12.461(3)$, $b = 15.198(6)$, $c = 12.920(2)$ Å, $\beta = 105.74(2)°$, $V = 2355.07$ $Å^3$, $Z = 4$, $D_m = 1.38$, $D_c = 1.378$ g cm^{-3}, $F(000) = 1008$, $\mu(M_0\ K_\alpha) = 2.3$ cm^{-1}, $R = 3.9$.

A total of 3672 independent reflections were measured to a maximum 2θ value of 50°. After application of Lorentz and polarization corrections, 3446 unique reflections with $[I \ge 2\sigma(I)]$ were used in the refinement. No absorption corrections were applied. The structure was solved by direct methods using SHELXS-86 [15] and refined to R index 0.041 by the full-matrix least-squares method using SHELXL-93 [16]. The hydrogens were fixed geometrically but not refined. The figure was drawn by PLUTO [17]. All the calculations were performed on a PC-486 computer.

ACKNOWLEDGMENT

The authors gratefully acknowledge the financial assistance from Hindustan Leaver Research Foundation, Bombay, India. BSR is thankful to the UGC, New Delhi, for financial assistance.

REFERENCES

[1] (a) J. D. Spivack: Brit. Patent, 2,087,399 (1982); *Chem. Abstr.* 97 (1981) 198374u; (b) K. Idel, H. J. Buysch, D. Margotte, H. Peters: Ger. Offen, 2,929,229 (1981); *Chem. Abstr. 94* (1981) 193200n; (c) M. Rasberger: U.S. Patent, 4,322,527 (1982); *Chem. Abstr.*

94 (1981) 191917c; (d) J. D. Spivack, L. D. Steinhuebel, *J. Heterocyclic Chem.*, *21*, (1984), 1285.

[2] Z. S. Ariyan, L. A. Wiles, *J. Chem. Soc.*, 1962, 3876.

[3] (a) L. C. Thomas, R. A. Chittenden, *Chem. Soc. (London)*, 1961, 1913; (b) L. C. Thomas: *The Interpretation of the Infrared Spectra of Organophosphorus Compounds*, Heydon, London, 1974.

[4] C. D. Reddy, R. S. Reddy, M. S. Reddy, M. Krishnaiah, K. D. Berlin, P. Sunthankar, *Phosphorus, Sulfur and Silicon*, *62*, 1991, 1.

[5] (a) C. D. Reddy, R. S. Reddy, C. N. Raju, M. El-Masri, K. D. Berlin, S. Subramanian, *Magn. Reson. Chem.*, *29*, 1991, 1140; (b) C. D. Reddy, K. D. Berlin, R. S. Reddy, C. N. Raju, M. ElMasri, S. Subramanian, *Phosphorus, Sulfur and Silicon*, *81*, 1993, 61.

[6] G. W. Buchanan, R. H. Wightman, M. Malaiyandi, *Org. Magn. Reson.*, *19*, 1982, 98.

[7] G. C. Levy, J. D. Cargioli, *J. Chem. Soc., Chem. Commun.*, 1970, 1663.

[8] (a) E. L. Eliel, V. S. Rao, K. M. Pietrusiewicz, *Org. Magn. Reson.*, *12*, 1979, 461. (b) G. E. Maciel, G. B. Savistzky, *J. Phys. Chem.*, *69*, 1976, 3925. (c) S. F. Nelson, G. R. Weisman, *J. Am. Chem. Soc.*, *98*, 1976, 3281.

[9] (a) G. W. Buchanan, D. A. Ross, J. B. Stothers, *J. Am. Chem. Soc.*, *88*, 1966, 4301; (b) D. M. Grant, B. V. Cheney, *J. Am. Chem. Soc.*, *89*, 1967, 5315.

[10] C. D. Reddy, C. V. N. Rao, D. B. Reddy, M. D. Thompson, J. Jasinski, E. M. Holt, K. D. Berlin, *Indian J. Chem.*, *24B*, 1985, 481.

[11] S. Maninaidu, M. Krishnaiah, K. Sivakumar, *Acta Crystallogr.*, *C48*, 1992, 483.

[12] S. Maninaidu: Ph.D. Dissertation, Sri Venkateswara University, Tirupati, India, 1990.

[13] K. Sivakumar, K. Subramanian, S. Natarajan, M. Krishnaiah, L. Ramamurthy, *Acta Crystallogr.*, *C45*, 1989, 806.

[14] S. Shanmuga Sundara Raj, M. N. Ponnuswamy, G. Shanmugam, S. Maninaidu, M. Krishnaiah, *Z. Kristallogr. 209*, 1993, 604.

[15] G. M. Sheldrick: *SHELXS-86, A System of Computer Program for Solution of Crystal Structures*, University of Gottingen, Germany, 1986.

[16] G. M. Sheldrick: *SHELXL-93, A System of Computer Program for Structure Refinement*, Institut fuer Anorg. Chemie, Germany, 1993.

[17] W. D. S. Motherwell: *PLUTO-1978, A Program for Plotting Molecular and Crystal Structure*, University of Cambridge, England, 1976. A version modified by W. Clegg, Anorganisch Chemisches Institut der Universitat Gottingen, Germany, 1978.