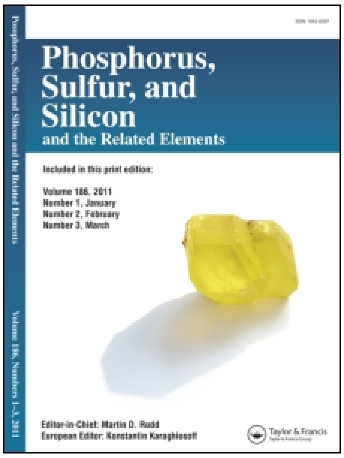

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SYNTHESIS OF 8-SUBSTITUTED-16*H*-DINAPHTHO [2,1-*d*:1',2'-g] 1, 3, 2-DIOXAPHOSPHOCIN 8-OXIDES

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SYNTHESIS OF 8-SUBSTITUTED-16*H*-DINAPHTHO [2,1-*d*:1′,2′-*g*]1,3,2-DIOXAPHOSPHOCIN 8-OXIDES

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A new family of phosphorus heterocycles, namely 8-substituted-16*H*-dinaphtho[2,1-*d*::1′,2′-*g*]1,3,2-dioxaphosphocin 8-oxides, has been obtained via a synthesis from reaction of bis(2-hydroxy-1-naphthyl)methane with a series of aryl phosphorodichloridates in dry benzene in the presence of triethylamine. NMR analysis of a solution of the title compounds revealed essentially no coupling between the bridged methylene protons and the P atom which suggested the dioxaphosphocin ring may exist in a boat conformation in solution. An X-ray diffraction analysis of a crystal of 8-(2′,3′-dimethylphenoxy)-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*]1,3,2-dioxaphosphocin 8-oxide does indicate that in the solid state the dioxaphosphocin ring is in a distorted and extended boat-like conformation with the P=O and bridged CH_2 groups directed away from each other. Electron impact mass spectral analysis confirmed the structures of the esters and showed M^+, $(M - R)^+$, and $(M - OR)^+$ ions containing the dioxaphosphocin ring system.

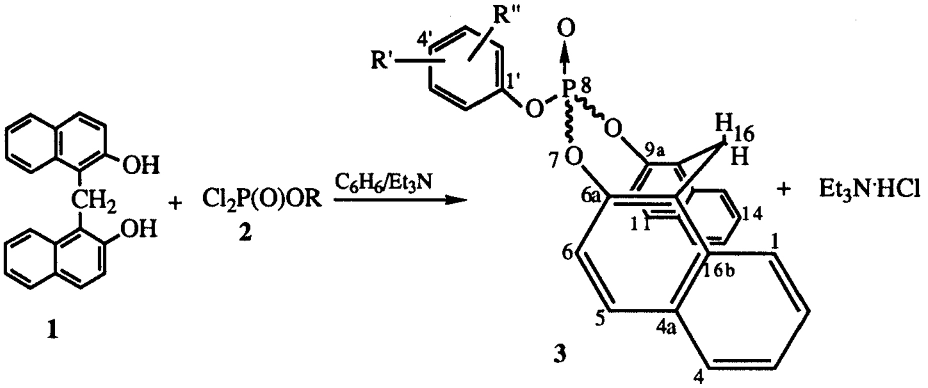
Key words: 8-Substituted-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*]1,3,2-dioxaphosphocin 8-oxides; NMR analysis; X-ray diffraction of 8-(2′,3′-dimethylphenoxy)-16*H*-dinaphtho[2,1-*d*:1′,2′-*g*]1,3,2-dioxaphosphocin 8-oxide; conformational analysis; mass spectral analysis.

INTRODUCTION

Conformational properties and molecular structure of phosphorus esters are often very important in terms of the many applications as pesticides.[1] The title compounds hold promise in this area and are a new class of phosphorus-containing heterocycles. Crystals suitable for a single X-ray diffraction analysis were found for **3h**. NMR analysis of H-1, C-13, and P-31 nuclei were applied to assess the major conformation(s) of the esters in solution. Mass spectral data were recorded for some of the systems.

RESULTS AND DISCUSSION

Bis(2-hydroxy-1-naphthyl)methane (**1**)[2] and aryl phosphorodichloridates[3] (**2**) react in dry benzene to give the title compounds **3** as shown below. Diol **1** in benzene was treated dropwise with members of **2** at room temperature over 0.5 hours after which time the mixture was heated at reflux for 6–12 hours. Interestingly, a similar reaction with arylphosphonic dichlorides required only 3–4 hours.[4] In the present study, thin layer chromatography was employed to follow the reaction. Anhydrous



[R' and R'' = H, CH_3, or Cl]

R

a. C_6H_5
b. 2'-$H_3CC_6H_4$
c. 3'-$H_3CC_6H_4$
d. 4'-$H_3CC_6H_4$

R

e. 3',4'-$(H_3C)_2C_6H_3$
f. 3',5'-$(H_3C)_2C_6H_3$
g. 2',6'-$(H_3C)_2C_6H_3$
h. 2',3'-$(H_3C)_2C_6H_3$

R

i. 2'-ClC_6H_4
j. 4'-ClC_6H_4
k. 4'-Cl-(2'-H_3C)C_6H_3
l. 4'-Cl-(3'-H_3C)C_6H_3

benzene was the best solvent both from the standpoint of solubility of reactants and by virtue of its boiling point which was below the thermal decomposition temperature of the esters **3**. Workup consisted of filtration of insoluble triethylamine hydrochloride followed by evaporation of the solvent. Recrystallization of the solid products from a suitable solvent afforded crystalline **3**. Reaction conditions, yields, elemental analysis, IR, and P-31 NMR shifts are in Table I. Appropriate H-1 NMR, C-13 NMR, and mass spectral data for some members of **3** are in Tables II, III, and IV, respectively.

The proton NMR spectrum of **3** showed only six signals in the region δ 6.90–8.47 (Table II). This suggests a symmetrical arrangement about the central dioxaphosphocin ring. Although the data correlated reasonably well with that reported[5] for similar protons in Naphthoxazin and certain dinaphtho-crown ethers, the corresponding protons in **3** were more downfield. This suggests a deshielding influence by a nearby group which could possibly arise from the phosphoryl function. The bridging methylene protons appear as two distinct doublets in the region δ 4.76–4.80 and 5.16–5.20 ($^2J_{H\text{-}H}$ = 16.1–16.5 Hz), indicative of the nonequivalence of the two protons. A search of the literature did not reveal *any* type of study on the class of compounds represented by **3**. However, one investigation[6] has been recorded on a few dioxaphosphocins in which a long range $^5J_{H\text{-}P}$ = 2.9 Hz was reported between one of the methylene protons and phosphorus. It was suggested that the lone electron pair on phosphorus was directed towards one of the protons as illustrated with conformation A. No such coupling was observed in the H-1 spectra of **3**. An examination of space-filling models suggests two possible strain-free conformations (B and C) for the dioxaphosphocin 8-oxide ring system in **3**. In conformer B there is a rigid chair while in conformer C a boat system exists with the P=O and CH_2 far apart. Actually, the models imply that the bulky naphthyl groups

TABLE I

Physical data for members of **3**

Compound (Formula)	MP (°C)	Reaction time (hrs)	Yield[a] (%)	Found (%) (Required)		IR (ν max) cm^{-1} [P-O-C(Ar)] (KBr)			^{31}P [NMR]
				C	H	P=O	O-C	P-O	^{31}P[e]
3a ($C_{27}H_{19}O_4P$)	170-172[b]	6	70	74.00 (73.97)	4.40 (4.34)	1300	1220	985	15.19
3b ($C_{28}H_{21}O_4P$)	184-185[b]	7	59	74.38 (74.34)	4.70 (4.65)	1300	1220	985	15.03
3c ($C_{28}H_{21}O_4P$)	188-189[b]	7	65	74.39 (74.34)	4.72 (4.65)	1310	1220	970	15.14
3d ($C_{28}H_{21}O_4P$)	207-208[b]	7	62	74.36 (74.34)	4.68 (4.65)	1300	1200	960	14.87
3e ($C_{29}H_{23}O_4P$)	204-206[c]	8	55	74.70 (74.68)	4.96 (4.94)	1310	1220	960	14.83
3f ($C_{29}H_{23}O_4P$)	210-212[c]	7	60	74.80 (74.68)	4.90 (4.94)	1300	1210	980	-
3g ($C_{29}H_{23}O_4P$)	210-212[c]	8	53	74.70 (74.68)	4.89 (4.94)	1300	1210	965	15.10
3h ($C_{29}H_{23}O_4P$)	230-231[c]	8	54	74.63 (74.68)	4.98 (4.94)	1300	1210	970	15.00
($C_{27}H_{18}ClO_4P$)	219-220[d]	8	52	68.60 (68.57)	3.85 (3.81)	1310	1220	960	-
3j ($C_{27}H_{18}ClO_4P$)	162-165[d]	6	60	68.62 (68.57)	3.86 (3.81)	1310	1220	970	15.14
3k ($C_{28}H_{20}ClO_4P$)	216-217[b]	7	56	69.10 (69.06)	4.20 (4.11)	1310	1220	985	-
3l ($C_{28}H_{20}ClO_4P$)	227-228[b]	6	61	68.95 (69.06)	4.31 (4.11)	1310	1210	975	15.13

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[a] Yields were reported after one crystallization. [b] Methanol-benzene (2:1). [c] 1-Butanol. [d] Tetrahydrofuran.

[e] ^{31}P chemical shifts were expressed in δ units from 85% H_3PO_4 as external standard.

TABLE II

H-1 NMR data for members of **3** (δ from TMS)[a]

Compd.	H(1, 15)	H(2, 14)	H(3, 13)	H(4, 12)	H(5, 11)	H(6, 10)	CH_2		R
							H_a	H_b	
3a	8.24 (8.3)	7.55 (8.4, 7.0)	7.45 (7.8, 7.3)	7.82 (8.3)	7.70 (8.8)	7.12 (9.1)	5.19 (16.4)	4.84 (16.3)	7.22-7.39 m (5H-Ar)
3b	8.23 (8.8)	7.53 (8.4, 7.0)	7.43 (7.8, 7.2)	7.79 (8.3)	7.69 (8.8)	7.08 (8.9)	5.18 (16.5)	4.83 (16.2)	7.13-7.24 m (4H-Ar) 2.36 s (3H-CH_3)
3c	8.25 (8.7)	7.55 (8.4, 7.0)	7.45 (7.4, 7.3)	7.82 (7.9)	7.71 (8.8)	7.13 (8.8)	5.19 (16.7)	4.84 (16.2)	7.04-7.29 m (4H-Ar) 2.35 s (3H-CH_3)
3d	8.23 (8.4)	7.54 (8.4, 7.0)	7.44 (7.7, 7.3)	7.81 (8.1)	7.70 (9.1)	7.05 (9.2)	5.19 (16.5)	4.84 (16.3)	7.04-7.09 m (4H-Ar) 2.45 s (3H-CH_3)
3e	8.23 (8.4)	7.52 (8.4, 7.0)	7.43 (7.6, 7.4)	7.80 (7.8)	7.70 (8.8)	7.14 (8.8)	5.16 (16.1)	4.83 (16.2)	7.09-7.10 m (3H-Ar) 2.23 s (6H-CH_3)
3f	8.24 (8.6)	7.54 (8.2, 7.0)	7.43 (7.8, 7.4)	7.82 (8.2)	7.70 (8.8)	7.13 (8.6)	5.16 (16.3)	4.82 (16.4)	7.10-7.26 m (3H-Ar) 2.34 s (6H-CH_3)
3g	8.23 (8.4)	7.54 (8.4, 7.0)	7.44 (7.7, 7.3)	7.81 (8.2)	7.69 (9.1)	7.05 (9.2)	5.18 (16.5)	4.84 (16.3)	7.04-7.22 m (3H-Ar) 2.45 s (6H-CH_3)
3h	8.24 (8.7)	7.52 (8.4, 7.0)	7.43 (7.3, 7.3)	7.81 (8.3)	7.70 (8.9)	7.10 (7.8)	5.18 (16.1)	4.83 (16.2)	7.04-7.30 m (3H-Ar) 2.30 s (3H-CH_3) 2.27 s (3H-CH_3)
3i	8.22 (8.4)	7.52 (8.3, 7.0)	7.43 (7.7, 7.4)	7.80 (7.9)	7.70 (8.7)	7.12 (9.1)	5.19 (16.5)	4.82 (16.2)	7.20-7.35 m (4H-Ar)
3j	8.20 (8.3)	7.53 (8.3, 7.0)	7.42 (7.7, 7.3)	7.80 (7.8)	7.69 (8.8)	7.11 (9.1)	5.16 (16.1)	4.80 (16.5)	7.27-7.37 m (4H-Ar)
3k	8.25 (8.8)	7.53 (8.4, 7.1)	7.42 (7.8, 7.2)	7.80 (8.3)	7.71 (8.8)	7.13 (9.0)	5.14 (16.2)	4.81 (16.4)	7.16-7.36 m (3H-Ar) 2.35 s (3H-CH_3)
3l	8.25 (8.8)	7.54 (8.5, 7.1)	7.46 (7.5, 7.2)	7.84 (8.3)	7.73 (8.8)	7.14 (9.1)	5.20 (16.5)	4.83 (16.5)	7.23-7.36 m (3H-Ar) 2.37 s (3H-CH_3)

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

TABLE III

C-13 NMR data for members of 3(δ from TMS)[a]

Carbon atom	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**[b]	**3g**	**3h**	**3i**	**3j**	**3k**[b]	**3l**
C (1,15)	127.4	127.4	127.4	127.4	127.3	-	127.3	127.4	127.3	127.4	-	127.4
C (2,14)	125.4	125.4	125.4	125.4	125.4	-	125.6	125.4	125.4	126.5	-	125.5
C (3,13)	123.4	123.4	123.4	123.4	123.4	-	123.4	123.4	123.5	123.5	-	123.3
C (4,12)	129.2	129.1	129.2	129.1	129.1	-	129.1	129.1	129.1	129.2	-	129.2
C (5,11)	129.0	128.9	129.0	128.9	128.8	-	128.9	128.9	128.9	128.9	-	129.0
C (6,10)	120.0 (5.3)	120.0 (5.4)	120.1 (5.2)	120.0 (3.2)	120.1 (5.2)	-	120.0 (5.5)	120.0 (5.5)	120.0 (6.1)	119.9 (5.3)	-	120.0 (5.2)
C (6a,9a)	148.7 (9.2)	148.7 (9.3)	148.7 (9.2)	148.7 (9.4)	148.7 (9.4)	-	148.8 (9.3)	148.8 (8.6)	148.8 (9.7)	148.8 (7.2)	-	148.7 (8.2)
C (15b, 16a)	128.5 (4.4)	123.5 (4.4)	123.5 (4.6)	123.5 (4.5)	123.5 (4.4)	-	123.5 (4.4)	123.4 (4.5)	123.4 (4.4)	123.5 (4.4)	-	124.3 (4.5)
C (4a,11a)	132.6	132.6	132.6	132.6	132.6	-	132.6	132.6	132.4	132.4	-	132.6
C (15c, 16b)	131.9	131.9	131.9	131.9	131.9	-	131.9	131.9	131.8	131.9	-	131.9
C (16)	23.6	23.6	23.6	23.5	23.5	-	23.4	23.5	23.4	23.4	-	23.5
C (1')	150.5	149.8	150.3	148.2 (7.5)	148.1	-	148.4	149.1	146.5 (7.9)	148.5 (9.3)	-	148.6 (6.4)
C (2')	120.4 (4.8)	129.4	120.9 (3.9)	120.0 (2.9)	120.2 (4.8)	-	130.3 (3.5)	128.2 (6.6)	130.7	121.7 (4.9)	-	122.7 (14.0)
C (3')	129.9	131.6	140.2	130.3	138.4	-	129.1	139.0	127.9	129.9	-	138.0
C (4')	125.7	125.7	126.5	135.4	134.0	-	125.4	126.2	126.4	131.1	-	131.3
C (5')	129.9	127.2	129.6	130.3	130.6	-	129.1	127.0	125.8	129.9	-	130.1
C (6')	120.4 (4.8)	123.5 (4.0)	117.2 (3.8)	120.0 (2.9)	117.3 (4.7)	-	130.3 (3.5)	117.5	121.0 (3.4)	121.7 (4.9)	-	118.9 (4.9)
2'-CH_3	-	16.38	-	-	-	-	-	-	-	-	-	-
3'-CH_3	-	-	21.3	-	-	-	-	-	-	-	-	-
4'-CH_3	-	-	-	20.7	-	-	-	-	-	-	-	-
3', 4'-CH_3	-	-	-	-	19.9, 19.1	-	-	-	-	-	-	-
2', 6'-CH_3	-	-	-	-	-	-	17.2	-	-	-	-	-
2', 3'-CH_3	-	-	-		-	-	-	12.5, 20.2	-	-	-	-

[a] Data in parentheses are coupling constants J_{PC} (in Hz). [b]Not recorded; **3f** and **3k** are positional isomers of **3e** and **3l**, respectively

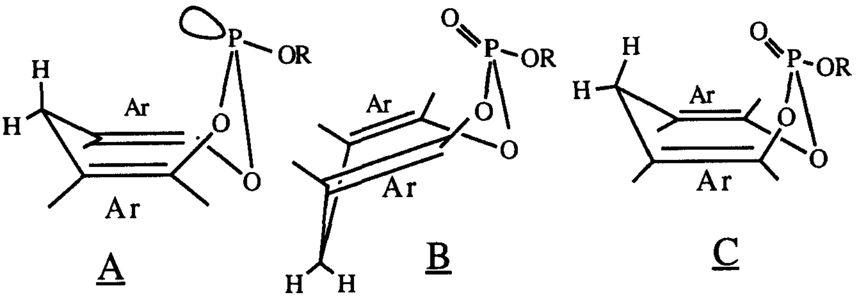
TABLE IV

Mass spectra (% of important ions) of certain members of 3[a]

Compd.	M^+ (Calculated)	M^+ (%) (Found)	$(M\text{-}R)^+$ 361	$(M\text{-}OR)^+$ 345	$(M\text{-}ROH)^+$ 344	$[(M\text{-}R)\text{-}PO_3H]^+$ 281	$[(M\text{-}OR)\text{-}PO_3H]^+$ 265
3a	438.1021	438.1023 (1.4)	0.4	1.8	3.5	7.5	1.4
3b	452.1177	452.1171 (8.1)	2.0	15.8	30.2	30.6	8.6
3c	452.1177	452.1203 (53)	11.5	9.3	21.3	22.4	5.6
3d	452.1177	452.1178 (0.9)	0.5	2.4	4.6	18.4	1.2
3e	466.1334	466.1326 (1.54)	0.4	3.7	8.9	11.8	1.8
3f	466.1334	466.1306 (0.5)	0.6	0.9	1.5	3.9	0.4
3g	466.1334	466.1374 (4.0)	1.1	6.8	14.8	15.1	3.2
3h	472.06311	472.0000 (7.0)	1.0	13.3	24	18	5
3i	472.06311	472.0453 (4.4)	1	12.7	22.6	22.5	5.8

[a]Data not recorded for **3j-3l** since they parallel that of **3i** and **3d**, respectively.

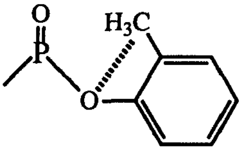
may force the CH_2 and P=O groups to be far removed from each other to minimize nonbonded interactions.



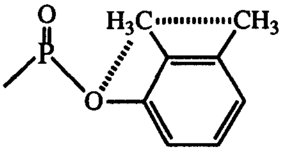
A B C

The ^{13}C NMR spectra exhibited ten signals which again implies a symmetrical molecule. Carbons 6, 6a, 9a, 10, 15b, and 16a experienced coupling with phosphorus (Table III). The range of $^2J_{P\text{-}O\text{-}C} = 7.4-11.4$ Hz is typical for C(6a) and C(9a) in related systems,[7] and, in our examples of **3**, the values were 7.2–9.7 Hz with the ^{13}C shift being 148.7 ppm. Shifts for C(6) and C(10) were at 120 ppm with the $^3J_{P\text{-}O\text{-}C\text{-}C} = 3.2-6.1$ Hz.[8] Due to the absence of a bonded hydrogen, low intensity signals for C(4a,11a) and C(15a,16b) were observed at 132.4–132.6 ppm and 131.8–131.9 ppm, respectively. Signals for C(3) and C(13) and for C(2) and C(4) appeared at 125.4 and 123.4, respectively, based to some degree on a comparison with carbons for dinaphtho crown ethers.[5] The remaining carbon signals were assigned on the basis of comparison with computed values for 1-methyl-2-naphthol.[4]

A doublet ($^2J_{POC(1')} = 6.9-9.2$ Hz) in the region 146.5–150.5 ppm was assigned to C(1′).[5] Both C(2′), and C(6′) showed coupling to phosphorus ($^3J_{POCC(2' \text{ or } 6')} = 2.9-4.9$ Hz).[8] The ^{13}C signals for C(2′) and C(6′) also appeared at the same position (117.2–130.7 ppm) in the absence of unsymmetrical substitution in the aryloxy group or of a group of C(4′). Substituents at various locations caused substantial variation in the shift for C(2′) or C(6′). There was a large upfield shift for the methyl group attached to C(2′) (as in **3b**) which was attributed to its interaction with an exocyclic oxygen.[7,9,10] In **3h**, there is additional shielding of the methyl group at C(2′) by 8 ppm, due possibly to the nonbonded interaction as illustrated. The same effect is present but is smaller in **3e** and **3l**.

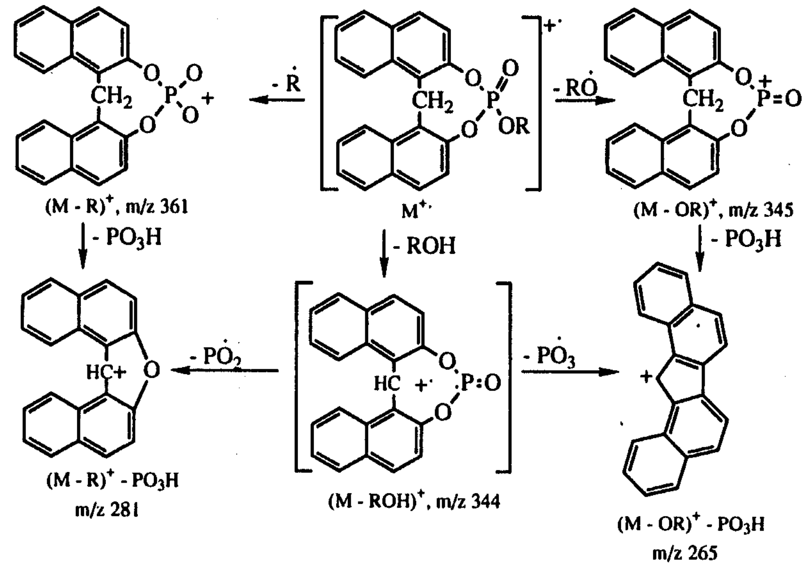


3b



3h

The ^{31}P NMR signals appeared in the range of −14.833 to −15.192 ppm. This is the apparent characteristic region for phosphorus shifts in the **3** systems.



SCHEME 1

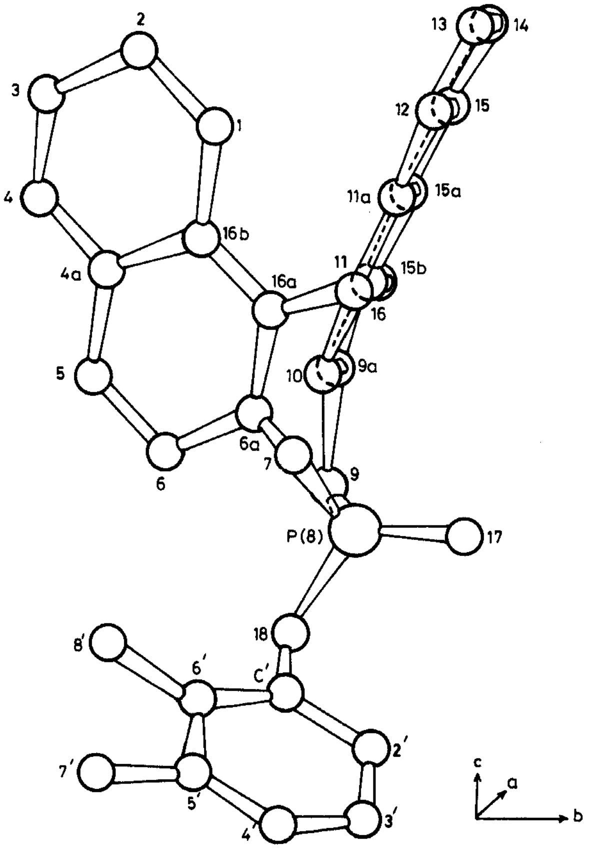


FIGURE 1 Perspective view of the molecule down 'a' axis.

High resolution electron impact mass spectra were recorded for some members of **3** (Table IV) exhibited $M^{+\cdot}$, $(M - R)^+$, and $(M - OR)^+$ uniformly,[11,12] thus supporting the proposed structures. This implies the dioxaphosphocin ring is reasonably stable at 70 ev. Other characteristic daughter ions are the xanthenium ion $[(M - R) - PO_3H]^+$ at m/z 281 and dibenzofluorenyl cation $[(M - OR) - PO_3H]^+$ at m/z 265 as shown in Scheme I.

The structure of crystalline **3h** was determined by X-ray diffraction analysis in an effort to establish the overall geometry of the system and to confirm the identity. Needle-like crystals were obtained from a solution in *n*-butanol. A view of the molecule **3h** down the 'a' and 'b' axes in Figures 1 and 2 show the atomic designation and the relative configurations of the asymmetric unit. Bond lengths and bond angles, excluding hydrogen, are found in Tables V and VI, respectively. While in the dioxaphosphocin ring system the *average* endocyclic and exocyclic P—O distance (1.581 Å) is comparable with the value of 1.587 Å of the dibenzodioxaphosphepin ring[13] in six- and seven-membered rings,[14–16] the P=O distance (1.476 Å) is slightly greater than the value (1.45 Å) found in the dibenzodithiaphosphepin ring.[17] This is probably due to bonding of the phosphorus with three additional electronegative oxygen atoms in the dioxaphosphocin ring. The lengthened endocyclic and exocyclic C—O bond (1.427 Å), when compared to the corresponding value of 1.406 Å of the dibenzodioxaphosphepin structure,[18] may be due to increased ring size. The large bond angles at C(6a), C(9a), and C(1') [126.8°, 124.8°, and 125.3°, respectively)] can be ascribed to the direct bonding of these carbon atoms to the electronegative oxygen atoms which are in turn bonded to the P=O group.

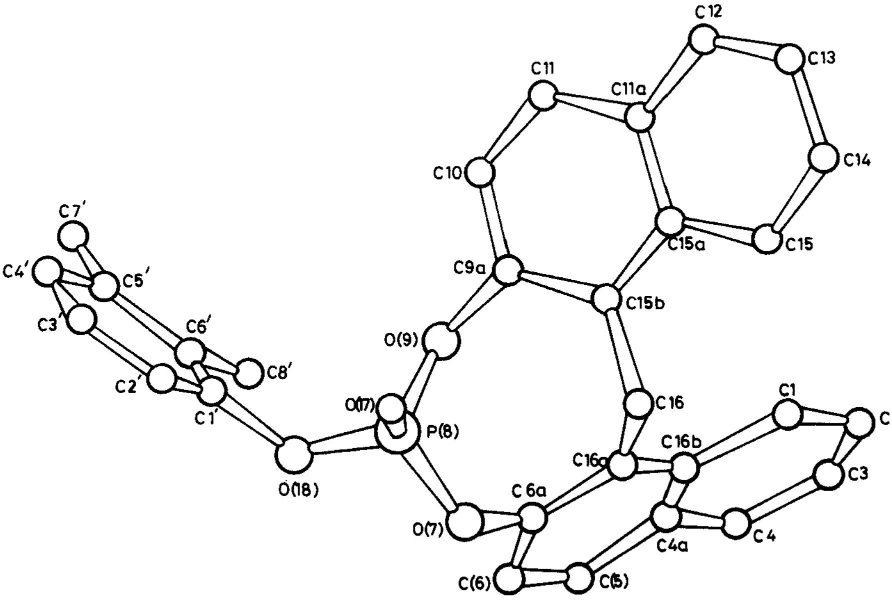


FIGURE 2 Perspective view of the molecule down 'b' axis.

TABLE V

Bond distances (Å) for **3h**. E. S. D.'s in parentheses

P(8) - O(7)	= 1.574(6)	C(15b) - C(15a)	= 1.445(8)
P(8) - O(9)	= 1.586(5)	C(15b) - C(9a)	= 1.365(10)
P(8) - O(18)	= 1.584(6)	C(15a) - C(15)	= 1.423(11)
P(8) - O(17)	= 1.476(5)	C(15a) - C(11a)	= 1.427(9)
O(7) - C(6a)	= 1.428(10)	C(15) - C(14)	= 1.392(11)
O(9) - C(9a)	= 1.418(8)	C(14) - C(13)	= 1.431(14)
O(18) - C(1')	= 1.435(11)	C(13) - C(12)	= 1.374(14)
C(6a) - C(6)	= 1.428(11)	C(12) - C(11a)	= 1.430(10)
C(6a) - C(16a)	= 1.338(9)	C(11a) - C(11)	= 1.409(12)
C(6) - C(5)	= 1.397(13)	C(11) - C(10)	= 1.370(9)
C(5) - C(4a)	= 1.404(11)	C(10) - C(9a)	= 1.417(9)
C(4a) - C(4)	= 1.437(12)	C(1') - C(6')	= 1.354(13)
C(4a) - C(16b)	= 1.443(10)	C(1') - C(2')	= 1.414(12)
C(4) - C(3)	= 1.365(12)	C(6') - C(5')	= 1.438(16)
C(3) - C(2)	= 1.453(12)	C(2') - C(8')	= 1.545(14)
C(2) - C(1)	= 1.407(12)	C(5') - C(4')	= 1.390(15)
C(1) - C(16b)	= 1.406(9)	C(3') - C(7')	= 1.562(17)
C(16b) - C(16a)	= 1.456(10)	C(4') - C(3')	= 1.433(16)
C(16a) - C(16)	= 1.523(10)	C(3') - C(2')	= 1.349(18)
C(16) - C(15b)	= 1.546(9)		

The dioxaphosphocin ring exhibits a boat-like conformation which is evident from the least squares mean plane and torsional angles (Figure 3). The heterocyclic ring experiences distortion due to bonding to the two naphthyl rings. Thus, the P=O group and methylene group are pointing in opposite directions at a maximum distance from each other. This orientation may be partially responsible for the lack of magnetic coupling (no $^4J_{PCH}$). The naphthalene groups I and II planes fused at C(6a)-C(16a) and C(15b)-C(9a), respectively, are at 126.2° and 26.6° to the plane of the heterocyclic ring. Both planes I and II are considerably away from each other with an angle of 104.7° to alleviate π-electron repulsions and short intramolecular contacts. The benzene ring is situated 94.4° below, but equidistant to, the plane of the heterocyclic ring and equidistant between the naphthalene rings. This conformation appears to have a minimum of nonbonded interactions.

In summary, we have developed a synthesis for the title compounds and have determined the structure of the solid state of one member. A boat arrangement exists for the heterocyclic ring with the P atom and the bridging methylene group at the bow-sprit positions.

TABLE VI

Bond angles (°) for **3h**. E. S. D.'s are in parentheses

P (8) - O (7) - C (6a)	= 119.7 (4)	C (15b) - C (15a) - C (11a)	= 118.8 (5)
O (7) - P (8) - O (9)	= 106.1 (3)	C (15a) - C (11a) - C (11)	= 120.4 (5)
P (8) - O (9) - C (9a)	= 121.9 (4)	C (11a) - C (11) - C (10)	= 120.9 (6)
O (7) - C (6a) - C (16a)	= 119.7 (5)	C (11) - C (10) - C (9a)	= 117.5 (5)
C (16a)- C (16) - C (15b)	= 112.5 (5)	C (15b) - C (9a) - C (10)	= 124.8 (5)
C (16) - C (15b) - C (9a)	= 121.6 (5)	C (15a) - C (15) - C (14)	= 119.9 (6)
O (7) - P (8) - O (18)	= 100.4 (3)	C (15) - C (14) - C (13)	= 121.3 (7)
O (9) - P (8) - O (18)	= 102.2 (3)	C (14) - C (13) - C (12)	= 119.1 (7)
O (9) - P (8) - O (17)	= 116.1 (3)	C (13) - C (12) - C (11a)	= 121.3 (6)
P (8) - O (18) - C (1')	= 106.1 (4)	C (15a) - C (11a) - C (12)	= 119.3 (6)
C (6) - C (6a) - C (16a)	= 126.8 (6)	C (1') - C (6') - C (5')	= 116.6 (7)
C (6a) - C (6) - C (5)	= 115.9 (6)	C (6') - C (5') - C (4')	= 120.2 (8)
C (6) - C (5) - C (4a)	= 120.1 (8)	C (5') - C (4') - C (3')	= 119.1 (8)
C (5) - C (4a) - C (16b)	= 121.5 (6)	C (4') - C (3') - C (2')	= 121.7 (8)
C (4a) - C (16b) - C (16a)	= 117.2 (6)	C (3') - C (2') - C (1')	= 117.0 (8)
C (4) - C (4a) - C (16b)	= 119.2 (6)	C (6') - C (1') - C (2')	= 125.3 (7)
C (4a) - C (4) - C (3)	= 121.5 (6)	C (4') - C (5') - C (7')	= 121.8 (8)
C (4) - C (3) - C (2)	= 121.5 (6)	C (5') - C (6') - C (8')	= 123.7 (7)
C (3) - C (2) - C (1)	= 120.2 (6)		
C (4a) - C (16b) - C (1)	= 121.3 (5)		

EXPERIMENTAL

The melting points were determined on a Mel-Temp apparatus and were uncorrected. Elemental analyses were performed by the Central Drug Research Institute, Lucknow, India. All IR spectra were recorded as KBr pellets on a Perkin-Elmer 683 unit while H-1, C-13 and P-31 NMR spectra were recorded on a Varian XL-300 spectrometer operating at 299.9 MHz for H-1, 75.43 MHz for C-13, and 121 MHz for P-31. All NMR data were taken on $DCCl_3$ solutions and were referenced from TMS (H-1 and C-13) or 85% H_3PO_4 (P-31). The C-13 spectra of **3f** and **3k** were not recorded since they are only positional isomers of **3e** and **3l**, respectively. Mass spectra were taken on a DS-505 mass spectrometer at 70 ev with a direct inlet system. The mass spectra of **3j**–**3l** were not recorded since it was assumed the decomposition pattern should parallel that found for the related systems which contained the single methyl or chlorine group.

8-Phenoxy-16H-dinaphtho[*2,1-d:1′,2′-g*]*1,3,2-dioxaphosphocin 8-oxide* (**3a**). The general procedure to obtain members of **3** will be illustrated by the synthesis of **3a**. Phenyl phosphorodichloridate [**2**, 2.1 g, 0.01 mole in a minimum of dry benzene] was added dropwise over a period of 30 minutes to a stirred solution of bis(2-hydroxy-1-naphthyl)methane [**1**, 3.0 g, 0.01 mole) and triethylamine (2.02 g, 0.2 mole) in dry benzene (80 mL). When the addition was complete, the temperature was slowly raised to reflux

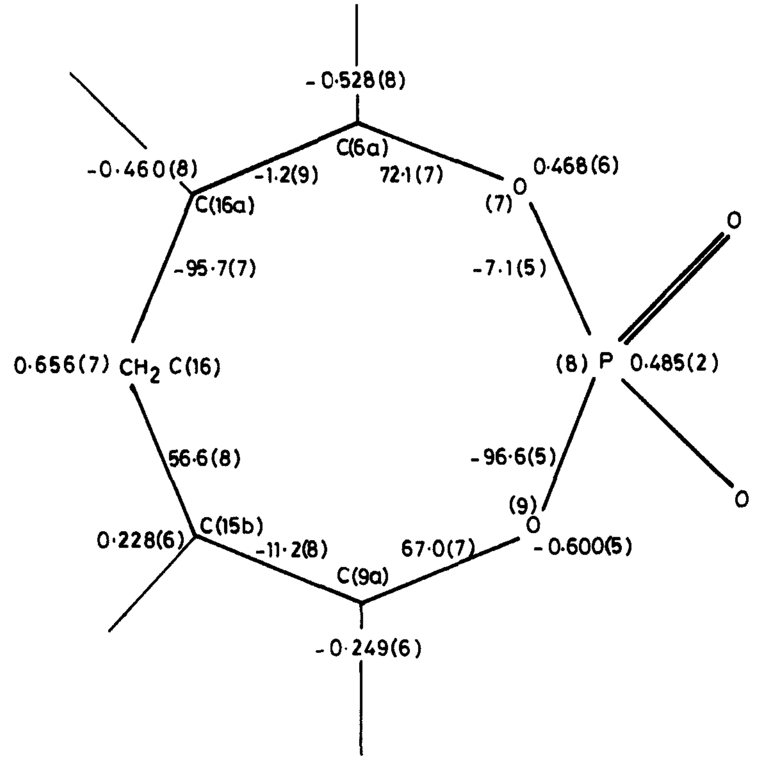


FIGURE 3 (a) Deviations of atoms from the mean plane through all the atoms are given in Å. (b) Torsion angles of the heterocyclic ring are given inside the ring in degrees. (c) c.s.d's are in parenthesis.

which was maintained for 6 h. Reaction progress was followed via TLC analysis with silica gel. Triethylamine hydrochloride separated rapidly from the mixture and was filtered at the end of the reaction period. Evaporation of the solvent left a residue which was washed with water and then recrystallized from methanol:benzene (2:1) to yield white crystals of **3a**. Esters **3b–3l** were obtained in a similar fashion. Spectral data are given in the respective Tables along with the elemental analyses.

Crystal Structure Determination. A colorless crystal with dimensions 1.0 × 0.5 × 0.3 cm^{-1} of **3h** was grown from a solution of *n*-butanol and was needle-like in shape. It was used for data collection with preliminary crystal data being determined via the 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: $C_{29}H_{23}O_4P$, MW = 466, monoclinic, space group $P2_1/c$, a = 12.245(1), b = 15.203(2), c = 13.147(2) Å, β = 106.22(09)°, V = 2350.1 $Å^3$, Z = 4, D_m = 1.34 g/cm^3, D_x = 1.317 g/cm^3, F(000) = 976, μ [monochromatic (graphite) Cu-K_α, γ = 1.5418 Å] = 12.94 cm^{-1}, R = 10.9.

A total of 4838 independent reflections were taken by the w/2θ scan technique with $2\theta < 120°$. After application of Lorentz and polarization corrections, 3782 reflections were found significant with $I > 3\sigma$ (I). No absorption corrections were applied. Multi-solution direct methods (MULTAN 80)[19] produced an E-map, set No. 5, which showed all nonhydrogen atoms except five atoms. The complete structure was developed from a few cycles of structure factor and Fourier synthesis. The structure was refined to R-index 0.109 by a least squares method where upon some hydrogen atoms were located from a difference map. Full-matrix least squares program SHELX-76[20] was used for the refinement. An R-factor of 10.9 was obtained by applying a unit weighting scheme and R_w was 12.2. Table VII lists the final postional parameters of non-hydrogen atoms.

TABLE VII

Final positional (fractional) parameters for non-hydrogen atoms in **3h**. E. S. D.'s are given in parenthesis ($\times 10^4$)

Atom	X	Y	Z
P(8)	6639 (2)	1113(1)	1875 (2)
O(7)	5571 (4)	0875(4)	2265 (4)
O(9)	7658 (4)	0540(3)	2571 (5)
O(18)	6332 (5)	0613(4)	0774 (4)
O(17)	6843 (4)	2069(3)	1860 (4)
C(6a)	5642 (6)	2069(5)	1860 (4)
C(6)	4991 (7)	-0579(6)	2563 (7)
C(5)	5006 (6)	-1274(6)	3262 (7)
C(4a)	5606 (5)	-1204(5)	4338 (6)
C(4)	5565 (6)	-1919(5)	5041 (7)
C(3)	6108 (6)	-1837(6)	6095 (7)
C(2)	6729 (6)	-1043(6)	6522 (6)
C(1)	6796 (5)	-0340(1)	5846 (6)
C(16b)	6237 (5)	-0421(5)	4760 (5)
C(16a)	6247 (5)	0288(5)	4018 (5)
C(16)	6878 (5)	1147(5)	4373 (6)
C(15b)	8140 (5)	1101(4)	4376 (5)
C(15a)	9037 (5)	1390(4)	5282 (5)
C(15)	8805 (6)	1747(5)	6200 (6)
C(14)	9698 (8)	2030(5)	7045 (7)
C(13)	10856 (8)	1947(6)	7025 (7)
C(12)	11083 (7)	1612(5)	6135 (7)
C(11a)	10187 (77)	1335(5)	5240 (6)
C(11)	10437 (6)	1028(5)	4319 (6)
C(10)	9586 (5)	0777(5)	3447 (6)
C(9a)	8449 (5)	0883(4)	3488 (5)
C(1')	7110 (7)	0603(5)	0136 (6)
C(6')	7576 (9)	-1077(6)	-0130 (7)
C(5')	8315 (9)	-0171(6)	-0692 (7)
C(4')	8453 (11)	0594(7)	-1222 (8)
C(3')	7886 (9)	1381(7)	-1048 (8)
C(2')	7250 (13)	1404(5)	-3600 (6)
C(8')	7288 (3)	-1012(6)	0531 (8)
C(7')	8933 (13)	-1045(8)	-0821 (10)

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