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Synthesis and ^1H, ^{13}C and ^{31}P NMR Studies of 2,10-Dichloro-6-aryloxy-12*H*-dibenzo[*d*,*g*][1,3,2]-dioxaphosphocin 6-Oxides

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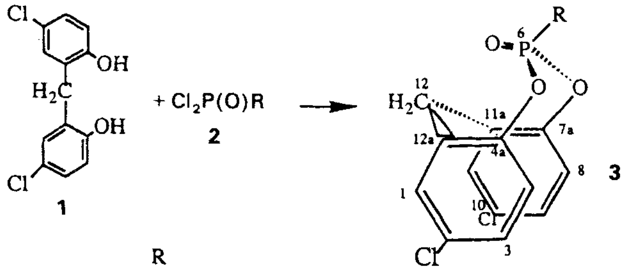
The spectral analyses and syntheses of several novel 2,10-dichloro-6-aryloxy/alkyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-oxides have been achieved. Long-range coupling [$^5J(H,P) = 2.4$ Hz] was observed between phosphorus and the bridged methylene protons. Based upon NMR data, a tub-like conformation is proposed for the central eight-membered dioxaphosphocin ring. Long-range $^2J(P,O,C)$ and $^3J(P,O,C,C)$ couplins were determined, as were the ^{31}P chemical shifts for sixteen members of these new heterocycles. A variable-temperature study of one member suggested the presence of a tub form as a reasonable candidate for one major conformer but the presence of other forms was also implied.

KEY WORDS ^1H, ^{13}C and ^{31}P NMR shifts 2,10-Dichloro-6-aryloxy-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-oxides

INTRODUCTION

2-Substituted-1,3,2-benzodioxaphosphole 2-oxides are not common but have been reported[1] as additives for lubricating oils, as antioxidants and as wear inhibitors. A few cyclic phosphorothiolates of saligenol are apparently useful as insecticides and fungicides.[2] 6-Substituted dibenzo[*d*,*f*][1,3,2]dioxaphosphepin 6-oxides[3–5] have been claimed to be fungicides, insecticides, bactericides, flame retardants, lubricants and stabilizers of polymers. In view of the potentially novel stereochemistry (tub, double chair, boat–chair of the phosphorus-containing ring and butterfly arrangement involving the two aryl rings), and various applications commonly associated with organophosphorus heterocyclics related to the above, the previously unknown title compounds were targeted for synthesis and examination by NMR analysis.



	R		
a	C_6H_5O	i	$4\text{-}ClC_6H_4O$
b	$2\text{-}H_3CC_6H_4O$	j	$4\text{-}Cl\text{-}3\text{-}(H_3C)C_6H_3O$
c	$3\text{-}H_3CC_6H_4O$	k	C_2H_5
d	$4\text{-}H_3CC_6H_4O$	l	$n\text{-}C_3H_7$
e	$3,4\text{-}(H_3C)_2C_6H_3O$	m	$i\text{-}C_3H_7$
f	$3,5\text{-}(H_3C)_2C_6H_3O$	n	$n\text{-}C_4H_9$
g	$2,6\text{-}(H_3C)_2C_6H_3O$	o	C_6H_{11}
h	$2\text{-}ClC_6H_4O$	p	C_6H_5

EXPERIMENTAL

NMR spectra were obtained in the Fourier transform mode on samples contained in 5 mm tubes (^1H and ^{31}P) or 10 mm tubes (^{13}C) on a Varian XL-300 NMR spectrometer with data acquisition at 299.94 MHz (^1H), 75.43 MHz (^{13}C) and 121.48 MHz (^{31}P). All spectra were recorded for solutions [30% (w/v) for ^1H and ^{31}P and 60–70 mg in 1 ml for ^{13}C] at 25 °C using $DCCl_3$ with TMS as the reference for ^1H and ^{13}C spectra and 85% H_3PO_4 for the ^{31}P spectra. All downfield shifts are on the δ scale from the standard and are labelled as positive. For ^{13}C, typical parameters were SW = 15085.9 Hz, PW = 17.7 μs (90°), acquisiton time = 1 s, spectral window = 20000 Hz, $D_1 = 3$ s. Signal-to-noise enhancement and baseline linearization were achieved by suitable exponential weighting and apodization of the free induction decay (FID).

Materials

The syntheses of compounds **3k–p** have been reported.[6] Melting points were determined on a Mel-temp apparatus and were uncorrected. Microanalyses were performed by the Central Drug Research Institute, Lucknow, India. IR spectra were recorded as KBr pellets on a Perkin–Elmer 137 spectrophotometer.

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2,10-Dichloro-6-(4-chlorophenoxy)-12*H*-dibenzo[*d,g*][1,3,2]-dioxaphosphocin 6-oxide (3i). The following procedure for **3i** is typical of that used for all previously unknown members of series **3**. 4-Chlorophenylphosphoro dichloridate (**2i**, 2.45 g, 0.01 mol) in dry toluene (20 ml) was added to a stirred solution of 5,5′-dichloro-2,2′-dihydroxydiphenylmethane (**1**, 2.69 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in toluene (60 ml). The mixture was heated at reflux with stirring for 4 h. Thin-layer chromatography was used to monitor the reaction. Filtration of the triethylamine hydrochloride produced a filtrate which was evaporated to a residue that, in turn, was washed with water and recrystallized [methanol–benzene (2:1)]. The yield of **3i** was 2.85 g (53%) of colorless crystals, m.p. 185–186 °C (analysis: calculated for $C_{19}H_{12}O_4Cl_3P$, C 51.64, H 2.72; found, C 51.60, H 2.74%). Mass spectral data, *m/z* (relative intensity, %): 444 (7.5, M + 4), 442 (20.4 M + 2), 441 (7, M + 1), 440 (21.6, $M^{+\bullet}$), 317 (9), 315 (41), 314 (27), 313 (49), 312 (29), 251 (33), 250 (10), 249 (49), 233 (17), 215 (30), 202 (12), 188 (11), 186 (34), 173 (16), 168 (19), 152 (38), 150 (29), 149 (16), 140 (13), 139 (44), 129 (42), 128 (100).

RESULTS AND DISCUSSION

The structures and numbering of positions are illustrated in the formulae shown. Table 1 contains the physical and IR data for **3a–j** and Table 2 shows the ^1H NMR signals (see also Table 1 in Ref. 6 for **3k–p**). The aromatic protons of the dioxaphosphocin moiety and aryloxy group absorb at δ 6.9–7.5 as a complex multiplet. However, the bridged methylene proton pattern consisted of a doublet, with $^2J(H,H) = 13.7–14.0$ Hz, at δ 3.84–3.91, or a doublet of doublets with $^2J(H,H) = 13.8$ and $J = 2.1–2.4$ Hz in the range of δ 4.06–4.16. Our contention is that the smaller coupling is a $^5J(H,P)$ due to long range interaction between the protons and phosphorus.[7] Space-filling models imply that a rigid, tub-like conformation is likely to be present for the eight-membered dioxaphosphocin ring, as illustrated. The rarity of this class of compounds does not permit a comparison with any valid model systems. It would seem intuitively reasonable that the tub-like arrangement as shown might permit through-space shielding, but coupling of phosphorus and a proton over five bonds is rare although not unknown.[8]

The ^{13}C chemical shifts are given in Tables 3 and 4. The interpretation of the data was based on additivity rules, C–P couplings, intensity of signals and SFORD spectra. A low-intensity doublet at δ 146.3–146.8 [^2J(P, O,C-4a) and ^2J(P,O,C-7a) = 8.0–11.5 Hz] was assigned to C-4a and C-7a,[9] which bear oxygen atoms. A doublet at δ 123.3–123.9 [^3J(P,O,C,C-4) and ^3J(P,O,C,C-8) = 4.1–5.2 Hz] was attributed to C-4 and C-8.[10] C-11a, 12a have signals at δ 132.7–133.9 [^3J(P,O,C-11a,12a) = 3.2–3.8 Hz]. The absorptions near δ 130 and that at δ 128.8 are attributed to C-1,11 and C-3,9, respectively. Chlorine-bearing carbons C-2,10 had signals at δ 131.0–131.9, while the bridgehead methylene carbon C-12 showed a resonance which averaged at δ 33.2. Although systems related to **3** are uncommon, it is interesting that a C-12 resonance is observed at δ 35.8 in a similar pentavalent, phosphorus-containing system.[11] No long-range ^4J(P,C) coupling was reported in this system,[11] although a ^5J(P,H) coupling (no value given) was noted. Thus, with a four-bond separation of C and P, the nature of the phosphorus atom may not have a large effect on the $\delta^{13}C$ values in these systems unless perhaps the atoms were forced into very close proximity to each other. The increased shielding of C-12 in our systems may well be the result of through space interaction with the P=O group, which lends credence to our suggestion that the heterocyclic ring is in a tub (or mantis-like boat) form.

Chemical shifts for the ^{13}C carbons in the aryloxy-P and alkyl-P groups for **3** are shown in Table 4. There is a partial correlation of shifts with those in peripherally related but simpler systems.[9,12] A doublet at δ 148.4–150.2 [^2J(P,O,C-1′) = 7 Hz] was assigned to C-1′ while C-2′,6′ also showed coupling to phosphorus, ^3J(P,O,C, C) = 4–7 Hz.[10] An upfield resonance of about 5 ppm for the H_3C group attached to C-2′ (as compared with signal for the methyl attached to C-3′ in **1f**, which appears at δ 21) is surely due to the γ-interaction with the exocyclic oxygen.[9,13,14] Consequently, the methyl

Table 1. Physical data[a] and IR bands of 3a–j

Compound	Formula	M.p. (°C)	Yield (%)	IR data (cm^{-1})		
				P=O	P—O—C (aryl)	
3a	$C_{19}H_{13}O_4Cl_2P$	158–159.5[b]	65	1280	1220	960
3b	$C_{20}H_{15}O_4Cl_2P$	137–138[c]	45	1290	1210	960
3c	$C_{20}H_{15}O_4Cl_2P$	140–141[d]	47	1285	1220	970
3d	$C_{20}H_{15}O_4Cl_2P$	134–135[c]	50	1290	1220	960
3e	$C_{21}H_{17}O_4Cl_2P$	152–153[d]	45	1295	1220	970
3f	$C_{21}H_{17}O_4Cl_2P$	194–195[b]	53	1300	1200	965
3g	$C_{21}H_{17}O_4Cl_2P$	162–163[c]	42	1295	1220	980
3h	$C_{19}H_{12}O_4Cl_3P$	174–175[d]	44	1300	1200	970
3i	$C_{19}H_{12}O_4Cl_3P$	185–186[d]	53	1297	1200	970
3j	$C_{20}H_{14}O_4Cl_3P$	164–165[d]	56	1295	1220	990

[a] *All compounds gave satisfactory C,H analyses. Data on esters* **3k–p** *have been reported elsewhere.*[6]

[b] Crystallized from propan-2-ol or anhydrous ethanol.

[c] Crystallized from methanol–benzene (2:1).

[d] Crystallized from butan-1-ol.

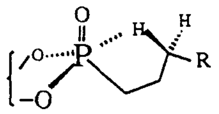
Table 2. ^{1}**H NMR data**^{a} **for 3a–j**

Compound	—CH_2—	Ar—H	O—Ar—CH_3
3a	3.81 (d, 13.5, 1 H) 4.11 (dd, 13.5, 2.4, 1 H)	6.99–7.43 (m, 11 H)	
3b	3.86–4.20 (m, 2 H)	6.92–7.32 (m, 10 H)	2.13 (s, 3 H)
3c	3.88 (d, 13.7, 1 H) 4.06 (dd, 13.8, 2.2, 1 H)	7.07–7.48 (m, 10 H)	2.15 (s, 3 H)
3d	3.91 (d, 14.0, 1 H) 4.08 (dd, 13.8, 2.3, 1 H)	6.93–7.51 (m, 10 H)	2.13 (s, 3 H)
3e	3.83 (d, 13.8, 1 H) 4.15 (dd, 13.8, 2.4, 1 H)	6.98–7.21 (m, 9 H)	2.23 (s, 3 H) 2.25 (s, 3 H)
3f	3.86 (d, 13.7, 1 H) 4.15 (dd, 13.8, 2.4, 1 H)	6.88–7.32 (m, 9 H)	2.33 (s, 6 H)
3g	3.90 (d, 14.0, 1 H) 4.10 (dd, 13.8, 2.2, 1 H)	6.95–7.45 (m, 9 H)	2.13 (s, 6 H)
3h	3.91 (d, 14.0, 1 H) 4.10 (dd, 11.7, 2.1, 1 H)	6.89–7.33 (m, 10 H)	
3i	3.86 (d, 13.7, 1 H) 4.16 (dd, 13.8, 2.1, 1 H)	7.00–7.40 (m, 10 H)	
3j	3.84 (d, 13.8, 1 H) 4.15 (dd, 13.8, 2.4, 1 H)	7.00–7.36 (m, 9 H)	2.38 (s, 3 H)

[a] Chemical shifts in ppm (from TMS) and *J* (Hz). Data on **3k–p** have been reported elsewhere.[6]

shifts are self-diagnosing in terms of designation of position in the aryloxy moiety.

Carbon resonances for the alkyl groups in **3k–o** are given in Table 4. All C-1′, C-2′ and C-3′ carbons experienced coupling with phosphorus, with averages for ^2J(P,C-1′), ^2J(P,C-2′) and ^3J(P,C-3′) being 140, 5.8 and 17.5 Hz, respectively. The significance of this high–low–high coupling profile has yet to be defined in P-alkyl systems of type 3, but may result, at least in part, from γ-type interactions as illustrated.



The ^{31}P resonances (Table 5) occurred from δ − 17.4 to − 18.2 for **3a–j**.[15–18] However, the derivatives **3k–o** had downfield signals at δ + 27.4 to + 30.3, which may also be appropriate for this family.[6,19] Variations in chain length of the alkyl group appeared to have little effect on the ^{31}P resonances, but branching of alkyl groups resulted in deshielding of phosphorus, such as seen with **3m**, which has an isopropyl group. The phenyl derivative **3p** had a signal at δ + 12.4, which agrees with that found in very simple systems.[18]

In view of the potentially dynamic nature of the system 3, it was deemed prudent to examine the behavior of one member, namely **3a**, over a wide temperature range. Since the geminal protons H-12_a and H-12_e (pseudo-axial and pseudo-equatorial, respectively) are

Table 3. ^{13}**C chemical shifts**^{a} **of dibenzodioxaphosphocin 6-oxides 3a–p**

Compound	C-1,11	C-2,10	C-3,9	C-4,8	C-4a,7a	C-11a,12a	C-12 (—CH_2—)
3a	130.1	131.6 (d, 2.4)	128.8	123.3 (d, 5.1)	146.5 (d, 7.9)	132.7 (d, 3.8)	32.8
3b	130.1	131.7 (d, 2.3)	128.9	123.5 (d, 5.1)	146.7 (d, 8.4)	132.9 (d, 3.6)	33.0
3c	130.2	131.7 (d, 2.4)	128.9	123.5 (d, 5.0)	146.7 (d, 8.0)	132.9 (d, 3.7)	33.0
3d	130.2	131.7 (d, 2.3)	128.9	123.5 (d, 4.9)	146.7 (d, 8.0)	132.9 (d, 3.7)	33.0
3e	130.2	131.7 (d, 2.2)	128.9	123.5 (d, 5.0)	146.8 (d, 8.0)	132.9 (d, 3.7)	33.0
3f	130.2	131.8^b	128.9	123.6 (d, 5.2)	146.8 (d, 8.7)	132.9	33.2
3g	130.1	131.7 (d, 2.4)	128.9	123.5 (d, 5.0)	146.7 (d, 8.3)	132.9 (d, 3.8)	33.1
3h	130.2	131.9 (d, 2.3)	128.9	123.4 (d, 5.1)	146.7 (d, 8.3)	132.7 (d, 3.8)	33.0
3i	130.2	131.9^b	129.0	123.4 (d, 4.1)	146.7 (d, 8.0)	132.8 (d, 3.3)	33.0
3j	130.3	131.9^b	129.0	123.5 (d, 4.3)	146.7 (d, 7.8)	132.8	33.1
3k	130.0	131.2 (d, 2.0)	128.7	123.8 (d, 4.2)	146.3 (d, 11.2)	133.7 (d, 3.1)	33.1
3l	130.0	131.2 (d, 1.9)	128.7	123.8 (d, 4.2)	146.3 (d, 11.2)	133.7 (d, 3.1)	33.1
3m	130.0	131.0^b	128.6	123.7 (d, 4.2)	146.4 (d, 11.5)	133.7 (d, 3.1)	33.2
3n	130.0	131.2 (d, 1.8)	128.7	123.8 (d, 4.2)	146.3 (d, 11.2)	133.7 (d, 3.2)	33.2
3o	130.0	131.0 (d, 1.8)	128.7	123.8 (d, 4.1)	146.4 (d, 11.5)	133.7 (d, 2.8)	33.2
3p	130.0	131.3 (d, 1.9)	128.8	123.9 (d, 4.4)	146.5 (d, 10.4)	133.5	33.3

[a] Chemical shifts in ppm (from TMS) and *J* (Hz).
[b] No splitting detected under the conditions applied.

Table 4. ^{13}C chemical shifts[a] of phenoxy and alkyl moieties in 3a–p

Compound	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C′(CH$_3$)
3a	150.0 (d, 6.9)	120.0 (d, 4.9)	129.9	125.9	129.9	119.9 (d, 4.9)	—
3b	148.8 (d, 7.3)	129.3 (d, 6.9)	131.6	125.8	127.2	119.5	15.95
3c	150.1 (d, 7.0)	116.9 (d, 4.7)	140.4	126.8	130.2	120.6 (d, 4.9)	21.3
3d	148.0 (d, 7.2)	119.7 (d, 4.9)	130.4	135.7	130.4	119.7 (d, 4.9)	20.7
3e	148.1 (d, 7.1)	117.0 (d, 4.6)	138.6	134.3	130.2	120.9 (d, 5.0)	19.1[b]
3f	150.2	117.5 (d, 4.5)	139.9	127.6	139.9	117.5 (d, 4.5)	21.2
3g	148.8 (d, 7.5)	129.3 (d, 6.9)	130.1	125.9	130.1	129.3 (d, 6.9)	—
3h	146.2 (d, 6.5)	125.7 (d, 7.3)	130.9	126.8	130.2	121.2 (d, 2.3)	
3i	148.5	121.4 (d, 3.9)	130.0	131.5	130.0	121.4 (d, 3.9)	—
3j	148.4 (d, 7.3)	122.4	138.2	131.6	130.3	118.7	20.2
3k	18.7 (d, 145.0)	8.4 (d, 7.3)					
3l	27.3 (d, 141.8)	16.1 (d, 5.7)	15.2 (d, J = 17.7)			—	—
3m	25.7 (d, 142.3)	15.9 (d, 5.3)				—	—
3n	25.1 (d, 130.9)	24.1 (d, 5.9)	23.6 (d, 18.0)	13.5	—	—	
3o	35.3 (d, 141.8)	25.6 (d, 4.8)	25.8 (d, 17.0)	26.0	25.8 (d, 17.0)	25.6 (d, 4.8)	—
3p	131.3	131.5 (d, 10.3)	128.6	128.8	128.6	131.5 (d, 10.3)	

[a] Chemical shifts in ppm (from TMS) and J (Hz).
[b] The 3-CH_3 appears at 19.9 ppm.

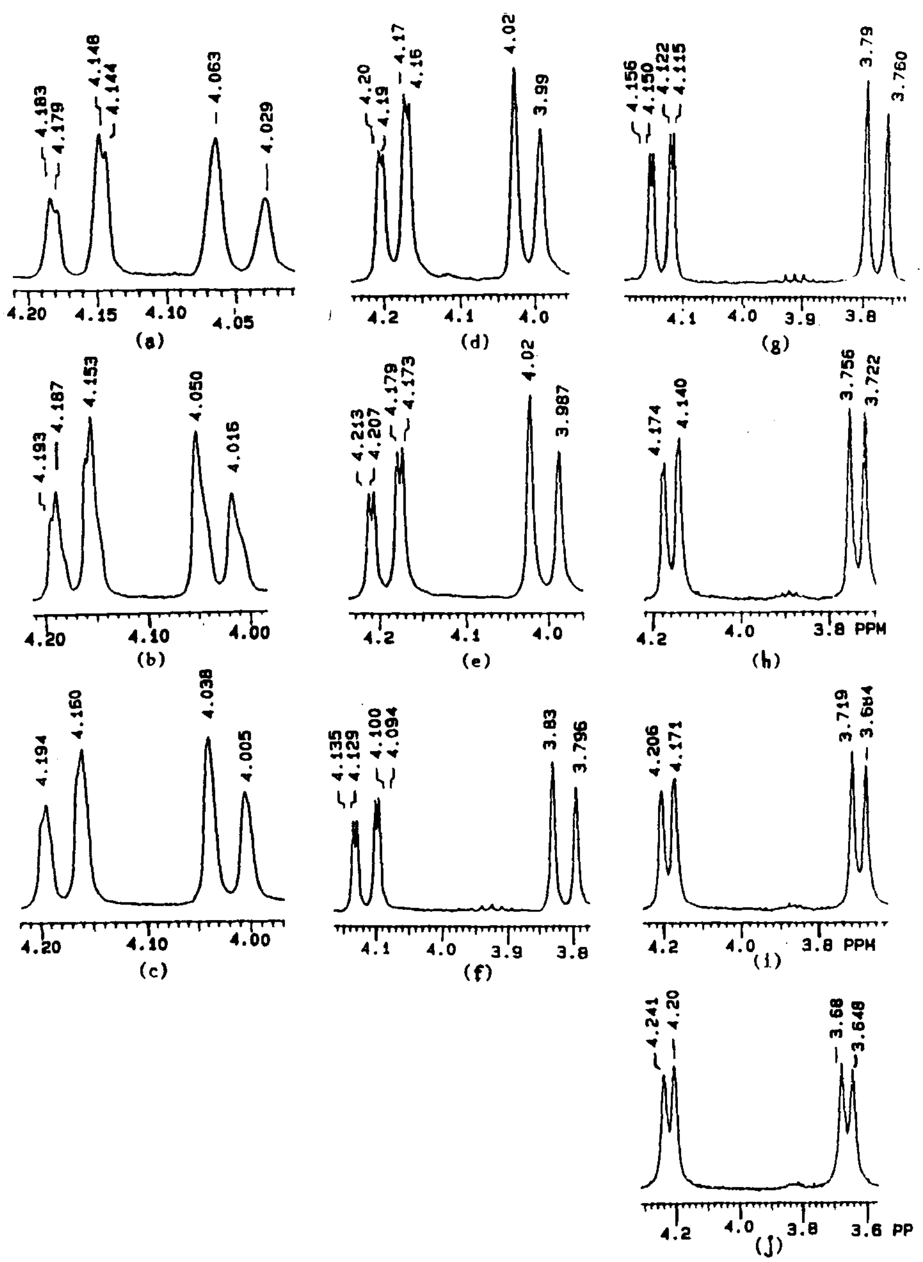


Figure 1. Variable-temperature study of **3a** at (a) 130, (b) 100, (c) 80, (d) 60, (e) 40, (f) 25, (g) 0, (h) −20, (i) −40 and (j) −60 °C.

Table 5. ^{31}P **chemical shifts**[a] **of 3a–p**

Compound	δ_P	Compound	δ_P
3a	−17.66	**3i**	−17.64
3b	—[b]	**3j**	−17.60
3c	−18.11	**3k**	+27.64
3d	−18.11	**3l**	+28.44
3e	−17.42	**3m**	+30.27
3f	−17.72	**3n**	+27.44
3g	−18.03	**3o**	+27.44
3h	−18.46	**3p**	+12.41

[a] Chemical shifts in ppm from 85% H_3PO_4.
[b] Chemical shift not recorded for **3b**.

Table 6. Chemical shift differences and couplings for H-12 in 3a as a function of temperature

Temperature (°C)	$\Delta\delta$ (ppm)	J (Hz)	$\Delta\delta/J$ (ppm Hz^{-1})
130	47	13.6	3.5
100	56	13.5	4.1
80	62	13.2	4.7
60	71	13.5	5.3
40	76	13.6	5.6
25	92	14.0	6.6
0	144	13.5	10.7
−20	167	13.5	12.4
−40	195	14.0	13.9
−60	224	12.8	17.5

attached to a bridging carbon of the eight-membered heterocyclic ring, ^1H NMR analysis might be revealing in terms of dynamic changes in the ring system. In Fig. 1, it is clear that the first-order AX pattern of the geminal protons displayed at or below room temperature degenerates into an AB pattern as the temperature is increased.[20] The $\Delta\delta/J$ values support this hypothesis, as can be seen in Table 6. Moreover, the intensities of the lower field doublet change sharply, indicating that the chemical shifts have been altered from the mid-point of the large doublet. Thus, the chemical shift was determiend using the equation $\delta_A - \delta_B = [(v_4 - v_1)(v_3 - v_2)]^{1/2}$. The dramatic change in the pattern on going from room temperature to 130 °C certainly implies a 'fluttering motion' in a 'butterfly'-type system in which more than one average conformer is seen over the range observed, since two coalescent points are observed for the lower field pattern for H-12. Cooling the system below room temperature to −60 °C shows another remarkable change which suggests that a preferred conformer is present. At the lower temperatures it is tempting to speculate that the major conformer has its phosphoryl group directed as in 3, since H-12_a is slightly *deshielded* compared with that observed at room temperature. The implication is that H-12_a lies in the deshielding region of the P=O group. Alternatively, if the PhOP=O moiety of the heterocyclic ring were 'bent' down between the two aryl rings, it would seem reasonable that H-12_a and H-12_e might approach magnetic equivalence in terms of chemical

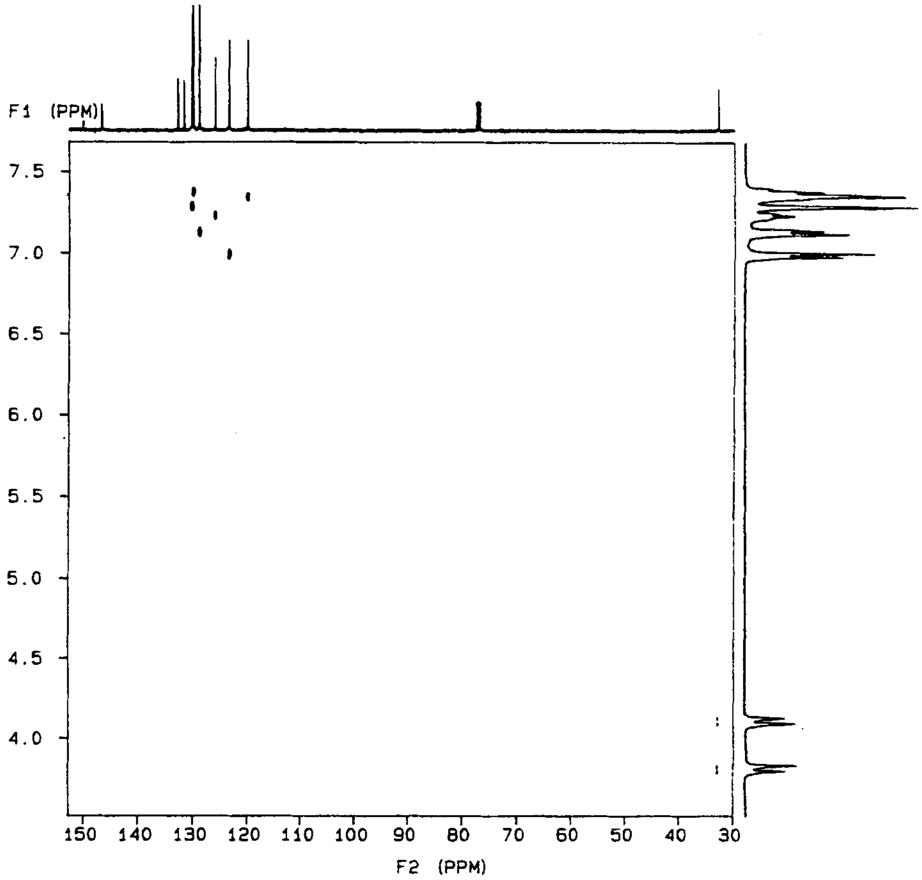
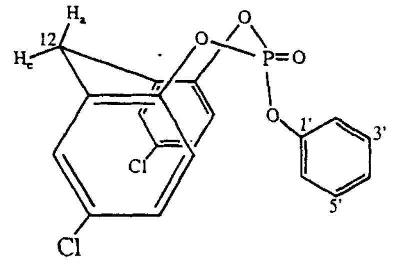


Figure 2. HETCOR 2D plot of **3a** at 25 °C.

shift since the two butterfly rings would expectedly be forced away from each other and into a more nearly planar arrangement. In fact, the Δδ values increase as the temperature is lowered, as seen in Table 6.



In contrast, and in support of this argument, is the observation that Δδ *decreases* as the temperature is elevated, suggesting that the average conformer has a more nearly planar heterocyclic ring system with the P=O group further removed from C-12 compared with the situation found at room temperature (a few other perpherally related butterfly-like phosphorus systems have been observed[21]). Interestingly, a variable-temperature study of **3a** from −60 to 130 °C produced ^{13}C NMR spectra which were nearly identical at all temperatures, except for C-12, which experienced subtle changes in shifts from 25 °C (30.95 ppm) to 130 °C (31.80 ppm) (in DMSO-d_6). A sharp change of 2.53 ppm was noted on going from 25 °C (32.78 ppm) to −40 °C (35.31 ppm) and nearly 3 ppm in continuing down to −60 °C (32.32 ppm) ($DCCl_3$). All such variations in chemical shifts suggest the involvement of more than one conformer and support the proton NMR data.

Irradiation of the aromatic protons in the ^{1}H spectrum of **3a** revealed that the small coupling in the lower field doublet of H-12 was *unaffected*, thereby confirming the ^5J(P,H-12) phosphorus coupling and that a ^4J(H,H-Ar) was *not* involved. Using appropriate offset frequencies for proton decoupling with respect to the signals for H-12, it was possible to observe the ^{31}P signal, which was greatly simplified. Thus, the coupling of both H-12 protons to phosphorus was confirmed. Moreover, irradiation at two offset frequencies in the aromatic proton region also resulted in simplification of the ^{31}P NMR signal (Fig. 2). Thus, the ^4J(P,H-4,8) coupling of an aromatic proton to phosphorus is substantiated.

A HETCOR 2-D plot of **3a** was generated (Fig. 3), from which it was possible to correlate most protons with a specific carbon by comparison with models, namely bis(phenoxyl)phosphorochloridate [$(PhO)_2P(O)Cl$] and bis(*o*-tolyloxy)phosphorochloridate [$(o\text{-}H_3CC_6H_4O)_2P(O)Cl$] (Aldrich). The absence of a carbon-bearing chlorine atom in the models allowed the identification of chlorinated carbons C-2,10 in **3a** at 131.6 ppm. This new signal differs from the singlets for C-1′, C-4a,7a and C-11a,12a, which are also non-proton-bearing carbons of low intensity (low NOE effects). The correlations discovered were as follows: δ 3.81 [H-12, ^3J(H,H) = 13.5 Hz] and 32.78 ppm (C-12), δ 6.99 [H-4,8, ^3J(H,H) = 8.5 Hz and ^4J(H,P) = 2.4 Hz] and 123.3 ppm (C-4,8), δ 7.13 [H-3,9, ^3J(H,H) = 8.6 Hz and ^5J(H,P) = 1.63 Hz] and 128.8 ppm (C-3,9), δ 7.23 [H-1,11, ^5J(H,P) = 1.1 Hz] and 130.1 ppm (C-1,11), and δ 7.25–7.4 (H-2′,3′,4′,5′,6′) and 120.0 (C-2′), 125.9 (C-4′), 129.9 (C-3′) and 150.0 (C-1′). These signals, and those at 146.5 and 132.7 ppm which were assigned to C-4a,7a and C-11a,12a, respectively, were diagnosed on the basis of comparison with the model systems.

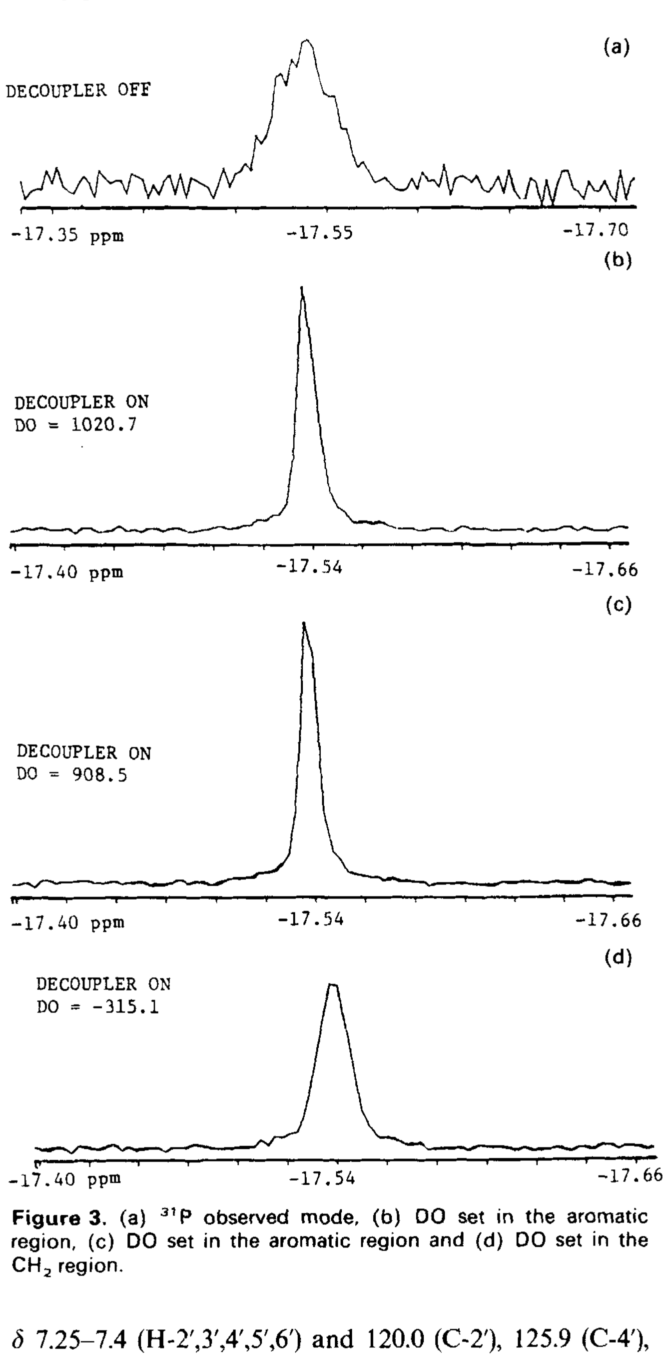


Figure 3. (a) ^{31}P observed mode, (b) DO set in the aromatic region, (c) DO set in the aromatic region and (d) DO set in the CH_2 region.

In conclusion, we have presented evidence that the title compounds possess eight-membered heterocyclic rings, each of which contains carbon, oxygen and phosphorus and is probably in a tub conformation. The ^{1}H, ^{13}C, ^{31}P and variable-temperature NMR studies on **3a** support the hypothesis for this rare class of phosphorus heterocyclics.

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