Tetrahedron, 1964, Vol. 20, pp. 2781 to 2795. Pergamon Press Ltd. Printed in Northern Ireland

CYCLIC ORGANOPHOSPHORUS COMPOUNDS—II[1]

THE INFRARED SPECTRA OF SOME 1,3,2-DIOXAPHOSPHORINANES

R. S. EDMUNDSON
Department of Chemical Technology, The Bradford Institute of Technology, Bradford

(*Received* 25 *June* 1964; *in revised from* 14 *August* 1964)

Abstract—The IR spectra of 47 1,3,2-dioxaphosphorinanes, mostly new compounds, have been recorded and discussed. Assignments have been made to P=O, P—O—C (alkyl and aryl), P=S and P—N stretching motions. In addition, it is suggested tentatively that multiple bands found at around 1000 to 1050 cm^{-1} and at around 1150 to 1200 cm^{-1} may be due to ring P—O—(C) vibrations.

RING systems containing phosphorus occur in nucleic acid, and are also involved as intermediates in a number of biological reaction sequences.[2] In addition, a number of medical and technological applications of such compounds have been summarized.[3] In view of this, and the continued interest in the synthesis of cyclic phosphorus compounds, it is surprising that no systematic accounts of the IR spectra of cyclic phosphorus esters and amides have yet appeared in the literature. Reports on the spectra of 1,3,2-dioxaphosphorinanes have been restricted to few compounds[1,2,4–11] and little has been attempted by way of correlation of spectral properties and size of the phosphorus-containing ring.[12,13]

Apart from their intrinsic interest, the spectra of the series of compounds I to IV were determined to aid in the study of bicyclic pyrophosphates derived from 2,2-dimethyl-propane-1,3-diol.[14]

EXPERIMENTAL

Materials. Benzene, toluene and ether were dried with Na. Triethylamine and pyridine were dried with BaO. 2,2-Dimethyl-propane-1,3-diol was dried by azeotropic distillation with benzene; other diols were dried over Na_2SO_4. Solutions of organophosphorus compounds were dried with

---

[1] Part I; R. S. Edmundson, *Chem. & Ind.* 1828 (1962).

[2] M. Eto, J. E. Casida and T. Eto, *Biochem. Pharmacol.* 337 (1962); M. Eto, S. Matsuo and Y. Oshima, *Agric. Biol. Chem. Japan* 27, 870 (1963).

[3] For a review, see; R. S. Edmundson, *Chem. & Ind.* 1770 (1962); see also; T. Nogrady and (Mrs.) K. M. Vagi, *J. Org. Chem.* 27, 2270 (1962); M. Eto, Y. Kinoshita, T. Kato and Y. Oshima, *Agric. Biol. Chem. Japan* 27, 789 (1963); M. Eto, K. Hanada, Y. Namazu and Y. Oshima, *Ibid.* 27, 723 (1963).

[4] R. L. McConnell and H. W. Coover, *J. Org. Chem.* 24, 630 (1959).

[5] A. G. Pinkus and P. G. Waldrep, *Chem. & Ind.* 302 (1962).

[6] K. D. Berlin, C. Hildebrand, J. G. Verkade and O. C. Dermer, *Chem. & Ind.* 291 (1963).

[7] K. D. Berlin, C. Hildebrand, A. South, D. M. Hellwege, M. Peterson, E. A. Pier and J. G. Verkade, *Tetrahedron* 20, 323 (1964).

[8] M. Eto and Y. Oshima, *Agric. Biol. Chem. Japan* 26, 452 (1962).

[9] R. Rätz and O. J. Sweeting, *J. Org. Chem.* 28, 1608, 1612 (1963).

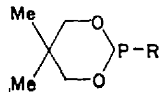
[10] W. S. Wadsworth jr. and W. D. Emmons, *J. Amer. Chem. Soc.* 84, 610 (1962).

[11] R. Burgada, *Thesis*, Paris (1963).

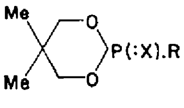
[12] J. Carson, W. N. Baxter and W. DeAcetis, *J. Org. Chem.* 24, 247 (1959).

[13] R. A. Y. Jones and A. R. Katritzky, *J. Chem. Soc.* 4376 (1960).

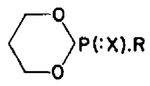
[14] For a preliminary report see; R. S. Edmundson, *Chem. & Ind.* 784 (1963).



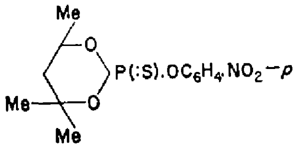
I



II



III



IV

anhydrous Na_2SO_4 or $MgSO_4$. Pet. ether had b.p. 60–80° unless otherwise stated. Distillations were carried out under N_2.

Phosphites. The preparation of 5,5-*dimethyl-2-ethoxy*-1,3,2-*dioxaphosphorinane* is typical. Ethanol (4·6 g) and pyridine (7·9 g) in ether (20 ml) were added to 5,5-dimethyl-2-chloro-1,3,2-dioxaphosphorinane[15] (16·8 g) in ether (50 ml) cooled in ice. The mixture was stirred for 0·25 hr, filtered, and the dried filtrate was distilled, yielding the *ester*. Physical properties for this, and other 5,5-dimethyl-2-alkoxy-1,3,2-dioxaphosphorinanes are listed in Table 1, comps 1 to 5.

Phosphates. Reaction between 2,2-dimethyl-propane-1,3-diol and methyl phosphorodichloridate in either ether or benzene in the presence of pyridine afforded poor yields of the cyclic *methyl phosphate*, (Table 1, No. 6), as did the oxidation of the corresponding phosphite in benzene with yellow mercuric oxide.[16] The compound was best prepared as follows. 5,5-Dimethyl-2-oxo-2-chloro-1,3,2-dioxaphosphorinane (11·2 g) dissolved in benzene (50 ml) was added to a suspension of sodium methoxide (from 1·39 g Na) in benzene (20 ml). After the vigorous reaction was over, the mixture was refluxed for 2 hr, cooled, washed with water, and the dried solution was evaporated. The product solidified after distillation.

The *isopropyl* and p-*nitrophenyl esters* were prepared similarly.

The *n-butyl phosphate* was prepared by the dropwise addition of a solution of 2,2-dimethyl-propane-1,3-diol (5·2 g) and pyridine (7·9 g) in ether (50 ml) to n-butyl phosphorodichloridate (9·6 g) in ether (20 ml). The final mixture was allowed to stand overnight and then worked up as for the methyl ester.

The *ethyl ester* was prepared similarly.

Thionophosphates. Sulphur (0·8 g) was added portionwise to 5,5-dimethyl-2-ethoxy-1,3,2-dioxaphosphorinane (4·45 g). The exothermic reaction was initiated by slight warming. After the reaction was complete, the resultant oil crystallized on standing at 0°. 5,5-*Dimethyl*-2-*thiono*-2-*ethoxy*-1,3,2-*dioxaphosphorinane* was recrystallized from ether. Table 1 lists this and other 2-thiono esters (Nos. 22 to 24) prepared in the same way.

Thiolophosphates. A solution of the triethylammonium salt of 5,5-dimethyl-2-thiono-2-hydroxy-1,3,2-dioxaphosphorinane[15] (5·7 g) and alkyl iodide (ca. 0·025 mole) in benzene, was heated over steam for 0·25 to 0·5 hr, and then worked up in the usual way. Two compounds (Table 1, Nos. 11 and 12) were so prepared.

Phosphoramidates. Compounds 14 to 21, and 33 to 35 (Table 1) were prepared as for 5,5-dimethyl-2-oxo-2-N-cyclohexylamino-1,3,2-dioxaphosphorinane.[15] If the compound tended to crystallize from the benzene solution during the working up procedure, the mixture was diluted with 1 vol. $CHCl_3$, and the working up continued (procedure A). A second procedure (B), using 2- moles of the primary amine, was also used in some cases.

Dithiophosphates. A suspension of the ammonium salt[17] of 5,5-dimethyl-2-thiono-2-thiolo-1,3,2-dioxaphosphorinane[15] (4·3 g) in dry acetone was boiled with alkyl halide (bromoethane; iodomethane and 2-iodopropane; ca. 0·025 mole) for 1 to 3 hr, and the final mixtures were poured into

---

[15] Preparation to be published.

[16] cf. L. Keay and E. M. Crook, *J. Chem. Soc.* 710 (1961).

[17] Dr. A. J. Lambie is thanked for a sample of this salt.

water. The precipitated solids were filtered off, air-dried, and then recrystallized. Table 1, compounds 25 to 27).

Phosphoramidothionates. A solution of 5,5-dimethyl-2-thiono-2-chloro-1,3,2-dioxaphosphorinane[15] (5·6 g) and the amine (0·025 mole) in benzene (20 ml) was heated over steam for 2 hr, and the cooled mixture was washed with water, dried, and then evaporated. The propyl compounds solidified and were recrystallized from pet. ether. The remaining compounds would not crystallize even after chromatography on alumina, and they were therefore distilled.

The compounds so prepared are listed in Table 1, Nos. 28 to 32.

Other compounds. The hydrogen phosphonate (II; $X = 0$, $R = H$) was prepared essentially as described by McConnell and Coover.[4] 2-Hydroxy- (No. 36) and 2-chloro- (No. 37) 5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane were prepared by modifications[15] of the literature[4] methods.

5,5-Dimethyl-2-oxo-2-phenyl-1,3,2-dioxaphosphorinane (II; $X = 0$, $R = Ph$; No. 38) m.p. 108·5–110° (from benzene; lit.[4] m.p. 115–116°), and 5,5-dimethyl-2-oxo-2-phenoxy-1,3,2-dioxaphosphorinane (II; $X = 0$, $R = OPh$; No. 39) m.p. 136–137° (from benzene; lit.[4] 133–135°) were prepared by the literature methods.

2,5,5-*Trimethyl*-2-*oxo*-1,3,2-*dioxaphosphorinane* (No. 40) was prepared by an Arbuzov rearrangement of the cyclic methyl phosphite. The action of alkyl halides on 2-alkoxy-1,3,2-dioxaphospholanes is known to bring about ring fission whereas with the corresponding dioxaphosphorinanes the ring may stay intact.[18] 5,5-Dimethyl-2-ethoxy-1,3,2-dioxaphosphorinane (0·65 g) and iodomethane (2·5 ml) were allowed to stand together for 7 days, and then warmed over steam for 15 hr. Removal of excess iodide left a solid which was recrystallized to give the desired methyl phosphonate (0·16 g, 27%) m.p. 119–121° from ethyl acetate-pet. ether. (Found: C, 44·2; H, 8·0; $C_6H_{13}O_3P$ requires: C, 43·9; H, 8·0%). The absence of OH stretching frequencies in the IR spectrum indicated that the product possessed a ring structure.

5,5-Dimethyl-2-thiono-2-chloro- (No. 41) and 5,5-dimethyl-2-thiono-2-thiolo-1,3,2-dioxaphosphorinane, II ($X = S$, $R = Cl$ and SH respectively; No. 42) are to be described in a future publication. 5,5-Dimethyl-2-thiono-2-p-nitrophenoxy-1,3,2-dioxaphosphorinane (No. 43) has already been described.[19]

Compound III; ($X = 0$, $R = Cl$; No. 44) had b.p. 106–109°/0·3 mm, m.p. 39–42°. 2-Oxo-2-phenoxy-1,3,2-dioxaphosphorinane (No. 45) had m.p. 73–74° (Lit.[20] m.p. 74–75°).

2-Thiono-2-*p*-nitrophenoxy- (No. 46) and 4,4,6-trimethyl-2-thiono-2-*p*-nitrophenoxy-1,3,2,-dioxaphosphorinane, IV (No. 47) have already been described.[19]

Compound XIV was prepared as described by Szmant and Emerson.[21] It had b.p. 69°/18 mm, $n_D^{19.5}$ 1·4468 (lit. b.p. 95°/40 mm, n_D^{20} 1·4450).

5,5-*Dimethyl*-2,2-*dioxo*-1,3,2-*dioxathiane* (XV). Attempts to oxidize the above cyclic sulphite with either yellow HgO in benzene, or with ammoniacal $AgNO_3$, were unsuccessful, although very slow reduction of the reagent did appear to take place. The compound was finally prepared by a modification of the procedure described by Brimacombe *et al.*[22] The cyclic sulphite (2·5 g) was added dropwise to a solution of $KMnO_4$ (9 g) and acetic acid (10 ml) in 400 ml water, and the solution was then stirred at 0° for 2·5 hr. It was then neutralized with $KHCO_3$, decolourized with $NaHSO_3$ and extracted repeatedly with ether. Evaporation of the dried extract yielded a solid which was recrystallized from pet. ether. The cyclic sulphate (2·0 g, 72%) had m.p. 79° (Lit. 79–80°).

Spectroscopy. Spectra were recorded using an Infracord spectrophotometer, Model 237. Measurements were made on samples of analytical purity, sometimes checked by vapour phase chromatography or paper chromatography. Solids were examined as KBr discs at concentrations of 0·25 to 0·75% w/w using pre-ground KBr, and with further grinding for approximately 30 sec. A disc of pure KBr was employed as a blank.

Pure liquids were examined as films between NaCl plates; solutions in standard NaCl cells.

---

[18] See for example; A. E. Arbuzov and M. M. Azanovskaya, *Izvest. Akad. Nauk. S.S.S.R.*, *Odt. Khim. Nauk* 473 (1949); A. E. Arbuzov and V. M. Zoroastrova, *Ibid.* 779 (1952); A. E. Arbuzov and N. A. Razumova, *Ibid.* 1061 (1958).

[19] R. S. Edmundson and A. J. Lambie, *Chem. & Ind.* 1048 (1959).

[20] D. C. Ayres and H. N. Rydon, *J. Chem. Soc.* 1109 (1957).

[21] H. H. Szmant and W. Emerson, *J. Amer. Chem. Soc.* **78**, 454 (1956).

[22] J. S. Brimacombe, A. B. Foster, E. B. Hancock, W. G. Overend and M. Stacey, *J. Chem. Soc.* 201 (1960).

TABLE 1

Compound no.	R	M.p. (°C) (B.p. °C/mm)	Yield (%)	Formula	Analyses (%)					
					Found			Calculated		
					C	H	P	C	H	P
Structure I										
1	OMe[1]	(66/18)	38	$C_6H_{13}O_3P$	43·6	7·55	18·9	43·9	8·0	18·9
2	OEt[2]	(76–77/16)	54	$C_7H_{15}O_3P$	—	—	17·35	—	—	17·35
3	OPr-n[3]	(85/15)	42	$C_8H_{17}O_3P$	49·6	8·4	16·0	50·0	8·9	16·1
4	OPr-i[4]	(74/15)	50	$C_8H_{17}O_3P$	49·4	9·05	15·8	50·0	8·9	16·1
5	OBu-n[5]	(98/14)	46	$C_9H_{19}O_3P$	52·0	9·3	14·8	52·4	9·3	15·0
Structure II (X = 0)										
6	OMe	94 (118–121/0·5)	57	$C_6H_{13}O_4P$	40·2	7·3	17·0	40·05	7·3	17·2
7	OEt	(94–95/0·3)[6]	50	$C_7H_{15}O_4P$	—	—	15·7	—	—	15·95
8	OPr-i	57–58 (136–139/3·5)	40	$C_8H_{17}O_4P$	46·3	8·4	14·9	46·15	7·2	14·9
9	OBu-n	(103/0·05)[7]	59	$C_9H_{19}O_4P$	48·5	8·65	13·85	48·6	8·6	13·95
10	$OC_6H_4NO_2$-p	124–125·5[8]	78	$C_{11}H_{14}NO_6P$	46·1	5·1	11·1	46·0	4·9	10·8
11	SMe	81–81·5[9]	54	$C_6H_{13}O_3PS$	36·45	6·8	15·8	36·7	6·7	15·8
12	SEt	42–44[10]	18	$C_7H_{15}O_3PS$	39·95	7·1	14·85	40·0	7·2	14·75
13	NMe_2	104·5–106[11]	39	$C_7H_{16}NO_3P$	42·85	8·0	16·05	43·5	8·3	16·0
14	NHPr-n	90·5–91·5[12]	69	$C_8H_{18}NO_3P$	45·95	8·7	15·1	46·3	8·75	14·9
15	NHPr-i	141–142[13]	82	$C_8H_{18}NO_3P$	45·8	8·2	15·2	46·3	8·75	14·9
16	NHBu-n	81–82[12]	68	$C_9H_{20}NO_3P$	48·35	8·95	13·75	48·9	9·1	14·0
17	NHBu-i	116–117[12]	18	$C_9H_{20}NO_3P$	48·8	9·05	14·0	48·9	9·1	14·0
18	NHBu-tert.	166[13]	57	$C_9H_{20}NO_3P$	49·0	9·0	13·8	48·9	9·1	14·0
19	NHAm-n	71–72[12]	63	$C_{10}H_{22}NO_3P$	51·3	9·4	14·0	51·05	9·4	13·15
20	NHAm-i	87·5–89[12]	70	$C_{10}H_{22}NO_3P$	50·45	9·2	14·3	51·05	9·4	13·15
21	NHHex-n	60–61[12]	55	$C_{11}H_{24}NO_3P$	52·75	9·5	12·4	53·0	9·7	12·4

Structure II (X = S)										
22	OMe[5]	93·5–94·5[9]	60	$C_6H_{13}O_3PS$	36·8	6·6	15·7	36·7	6·7	15·8
23	OEt	62–63[9]	50	$C_7H_{15}O_3PS$	—	—	14·85	—	—	14·7
24	OPr-n	(90–94/0·25)[14]	55	$C_8H_{17}O_3PS$	42·6	7·55	13·85	42·8	7·7	13·8
25	SMe	85·5–86[12]	81	$C_6H_{13}O_2PS_2$	34·55	6·15	14·15	33·95	6·2	14·6
26	SEt	69·5–70·5[12]	54	$C_7H_{15}O_2PS_2$	37·5	6·5	13·35	37·2	6·7	13·7
27	SPr-i	108·5[13]	17	$C_8H_{17}O_2PS_2$	40·25	7·0	12·85	40·0	7·1	12·9
28	NHPr-n[5]	70–70·5[12]	78	$C_8H_{18}NO_2PS$	43·1	8·25	13·1	43·0	8·1	13·9
29	NHPr-i	97·5–98·5[12]	75	$C_8H_{18}NO_2PS$	42·6	7·9	13·7	43·0	8·1	13·9
30	NHBu-n	(106–108/0·2)[15]	67	$C_9H_{20}NO_2PS$	45·2	8·4	13·55	45·5	8·5	13·05
31	NHBu-i	(90/0·05)[16]	51	$C_9H_{20}NO_2PS$	45·3	8·25	13·9	45·5	8·5	13·05
32	NHHex-n	(133/0·2)[17]	76	$C_{11}H_{24}NO_2PS$	49·6	9·1	11·75	49·8	9·1	11·7
Structure III (X = 0)										
33	NHBu-i	82·5–83[11]	28	$C_7H_{16}NO_3P$	43·5	8·2	15·95	43·5	8·35	16·0
34	NHBu-tert.	131–133·5[18]	64	$C_7H_{16}NO_3P$	43·65	8·4	15·3	43·5	8·35	16·0
35	NHC_6H_{11}-cyclo	152–153[13]	59	$C_9H_{18}NO_3P$	49·55	8·25	14·15	48·9	8·2	14·0

Notes on Table 1

[1] n_D^{18} 1·4424; [2] n_D^{22} 1·4420; [3] n_D^{21} 1·4481; [4] n_D^{18} 1·4388; [5] n_D^{18} 1·4463; [6] $n_D^{24·5}$ 1·4401; [7] n_D^{20} 1·4428; [8] from toluene; [9] from ether; [10] from ether–pet. ether; [11] from ethyl acetate–pet. ether; [12] from pet. ether; [13] from benzene–pet. ether; [14] n_D^{24} 1·4754; [15] n_D^{21} 1·4995; [16] n_D^{23} 1·5000; [17] n_D^{21} 1·4942; [18] from chloroform pet. ether.

TABLE 2. IMPORTANT ABSORPTION FREQUENCIES

Compound	$\nu_{P=O}$	$\nu_{P=S}$	ν_{P-O-C}		ν_{P-N}	ν_{N-H}
(1)	—	—	1066 s	1183 w	—	—
			1035 s			
			1008 s			
(2)	—	—	1065 s	1164 w	—	—
			1040 s			
			1009 s			
(3)	—	—	1055 s	1191 vw	—	—
			1043 s	1167 vw		
			1010 s	1152 w		
(4)	—	—	1060 s	1180 w	—	—
			—	1168 (sh)		
			1016 s			
(5)	—	—	1056 s	1168 (sh)vw	—	—
			1040 m	1148 (sh)vw		
			1030 m			
			1010 s			
(6)	1290 s	—	1072 s	1189 m	—	—
			1046 s			
			1012 s			
(7)	1298 s	—	1072 s	1168 w	—	—
			1042 s			
			1010 s			
(8)	1287 s	—	1060 s	1185 m	—	—
			1018 m			
			1003 s			
(9)	1300 s	—	1077 s	1153 m	—	—
			1058 s			
			1039 s			
			1033 s			
			1010 s			
(10)	1305 s	—	1057 s	1174 m	—	—
			—			
			1006 s			
(11)	1273 s	—	1052 s	1184 m	—	—
			—			
			1002 s			
(12)	1293 (sh) s	—	1064 s	1186 vw	—	—
	1278 s		1057 s			
	1266 (sh) s		1004 s			
(13)	1238 s	—	1070 m	1184 m	706 m	—
			1050 s			
(14)	1243 s	—	1060 s	1186 w	756 m(?)	3215 s
	1229 s		—	1134 m		
			1010 s			
(15)	1230 s	—	1056 s	1171 m	750 m(?)	3180 s
			—	1146 m		
			1004 s			
(16)	1233 s	—	1069 s	1186 w	734 w(?)	3180 s
			1054 s			
			—			
			1010 s			

TABLE 2 (*contd.*)

Compound	$\nu_{P=O}$	$\nu_{P=S}$	ν_{P-O-C}		ν_{P-N}	ν_{N-H}
(17)	1233 s	—	1070 s	1188 w	(?)	3190 s
			1054 s			
			1051 s			
(18)	1266 s	—	1061 s	—	(?)	3210 s
			1042 s			
			1026 s			
			1012 s			
(19)	1230 s	—	1066 s	—	736 w(?)	3180 m
			1056 s			
			—			
			1012 s			
(20)	1238 s	—	1066 s	1188 (sh) s	(?)	3190 s
			1058 (sh) s			
			—			
			1015 s			
(21)	1239 s	—	1058 s	1188 (sh) s	(?)	3240 s
			—			
			1008 s			
(22)	—	649 s	1058 s	1183 m	—	—
			1038 s			
			—			
(23)	—	650 m	1056 s	1161 m	—	—
			1036 s			
			—			
(24)	—	658 m	1062 s	1156 vw	—	—
			1051 s			
			1000 s(?)			
(25)	—	687 s	1049 s	1184 vw	—	—
			991 s(?)			
(26)	—	681 s	1049 s	1183 vw	—	—
			992 s(?)			
(27)	—	688 s	1062 s	1186 vw	—	—
			1042 s	1160 w		
			990 s(?)			
(28)	—	644 s	1056 s	1188 vw	750 m	3500–3300 s
			1043 (sh) s			
			1006 s			
(29)	—	650 s	1073 s	1188 w	787 s	3325 m
			1058 s	1169 m		
			1007 s			
(30)	—	644 m	1056 s	—	737 w	3440 (sh)
			1007 s			3300 m
(31)	—	648 m	1054 s	1188 vw	691 w(?)	3440 (sh) m
			1004 s	1183 vw		3300 m
(32)	—	646 w	1057 s	1188 (sh) m	727 vw	3440 (sh)
			—			3370 (sh)
			1006 s			3300 m
(33)	1258 (br) s	—	1053 (br) s	1175 vw	738 m(?)	3220 s
	1233 (br) s					
(34)	1258 s	—	1064 (br) s	1172 w	737 w	3205 s
	1248 s		1048 s			
	1233 (br) s		1026 s			

TABLE 2 (*contd.*)

Compound	$\nu_{P=O}$	$\nu_{P=S}$	ν_{P-O-C}		ν_{P-N}	ν_{N-H}
(35)	1256 s	—	1060 s	1190 vw	?	3200 s
	1237 s					
(36)	1223	—	1005 s	—	—	—
(37)	1305 s	—	1052 s	1185 w	—	—
			—			
			1005 s			
(38)	1278 m	—	1069 w	1180 w	—	—
			1056 w	1166 w		
			1015 w			
(39)	1285 s	—	1050 s	1166 m	—	—
			1028 m			
			1003 s			
(40)	1260 s	—	1056 s	1188 w	—	—
			1010 s			
(41)	—	687 s	1041 s	?	—	—
		678 s				
(42)	—	716 s	1042 s	1182 m	—	—
		684 s		1163 w		
(43)	—	680 m	1046 s	1184 w	—	—
			1002 s	1166 m		
(44)	1303 s	—	1042 s	—	—	—
(45)	1295 s	—	1037 s	1166 m	—	—
	1276 s		1022(sh) s	1158 m		
			1000 w			
(46)	—	678 s	1027 s	1193 (sh)	—	—
			1007 m	1157 m		
(47)	—	698 m	1046 s	1166 m	—	—
			1002 s	1151 m		

TABLE 3. SPECTRA OF CYCLIC SULPHITE AND SULPHATE

5,5-Dimethyl-2-oxo-1,3,2-dioxathiane. 2965 m, 2880 w, 1471 m, 1452 w, 1397 w, 1375 w, 1311 vw, 1235 vw, 1206 m, 1190 s, 1036 m, 977 s, 949 m, 919 w, 895 m, 790 m, 740 s, 679 s, 646 m.

5,5-Dimethyl-2,2-dioxo-1,3,2-dioxathiane. 2985 m, 2955 w, 2920 vw, 2890 vw, 1479 m, 1467 m, 1461 m, 1445, 1406 s, 1390 s, 1375 m, 1369 m, 1348 w, 1310 w, 1289 w, 1200 s, 1037 m, 961 s, 955 s(sh), 917 w, 898 m, 826 s, 786 m, 777 m, 658 m.

The following abbreviations are used in the Tables: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. Brackets indicate a doublet.

RESULTS AND DISCUSSION

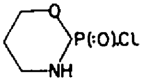
The principal band assignments are incorporated into Table 2.

The 3500 *to* 3000 cm^{-1} *region.* The main interest in this region lies in the assignment of NH stretching frequencies for the phosphoramidates and their thiono analogues, and the OH frequencies for the acid (No. 36). Both groups of phosphoramidates, independently of substitution in the ring, give one or more bands within this region. The 2-oxo phosphoramidates are characterized by a single, sharp, strong band at 3220–3180 cm^{-1}, assigned to the NH stretching motion, lowered from the normal 3500–3300 cm^{-1} region, either by hydrogen bonding or by the physical state of the compounds.[23] The former would seem to be the more likely in view of the normal

---

[23] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*. Methuen, London (1958).

values found for the solid phosphoramidothionates (Nos. 28 and 29). No systematic trends are observable in the values for ν_{NH} for the phosphoramidates (Nos. 14 to 21), and even the tertiary butyl group does not bring about any pronounced change in frequency or intensity of this band. The C–5 gem-dimethyl group also appears to have little influence on ν_{NH} as evidenced by comparison of the spectra of corresponding derivatives of propane-1,3-diol and 2,2-dimethylpropane-1,3-diol.[24] Construction of models indicates that given the right conformation, interaction between the alkyl groups at C–5 and groups attached to the phosphorus atom could be quite marked. Iwamoto and his colleagues[25] also found that ring compounds possessing NH joined to ring phosphorus e.g. compound V, are associated judging by the low stretching frequency observed (3135 cm^{-1}) in Nujol mulls. When exocyclic NH bonds were also present, a further band at 3333 to 3236 cm^{-1} is to be found.



V

The NH stretching bands in the phosphoramidothionates are generally weaker and also broader, than those for the oxygen analogues. Moreover, absorption lies nearer to the normal frequency. In addition, it is interesting to note that the spectra of 5,5-dimethyl-2-thiono-2-N-n-butylamino- and 5,5-dimethyl-2-thiono-2-N-isobutylamino-1,3,2-dioxaphosphorinane show a very weak, but sharp, band at 3590 cm^{-1}. A preliminary examination of two compounds, namely 5,5-dimethyl-2-oxo-2N-n-propylamino- (No. 14) and 5,5-dimethyl-2-thiono-2-N-n-butylamino-1,3,2-dioxaphosphorinane (No. 30) in solution, has been carried out. The latter compound was examined in carbon tetrachloride solution over the concentration range 0·5 to 9% w/w. Decrease in concentration led to the disappearance of the broad band at ca. 3300 cm^{-1} much more quickly than the sharp band at 3440 cm^{-1}. Variation of the concentration of the N-n-propylphosphoramidate solution between 0·4 and 2% showed no alteration in the position of the very strong, sharp band at 3445 cm^{-1} nor to the position of the broad band at 3220 cm^{-1}. The results indicate a greater degree of hydrogen bonding in the phosphoramidates than in the phosphoramidothionates, and imply that in such rigid cyclic structures as those under consideration, the sulphur atom is sufficiently large to prevent molecules approaching closely enough for intermolecular hydrogen bonding to occur. Exceptions to this would be those compounds having only small alkyl groups attached to the nitrogen atom, particularly in the solid state. It may be noted that the NH band for the N-n-propyl phosphoramidate is broad, while that for the N-isopropyl compound is very sharp.

Aromatic CH stretching frequencies occur at the normal positions, and in all cases (Compounds 10, 38, 39, 43, 45, 46 and 47) are weak.

A strong broad band at around 3400 to 3250 cm^{-1} exhibited by the cyclic phosphoric acid (No. 36) is probably due to bonded hydroxyl groups in a polymeric structure in the solid state.[26]

---

[24] For 5,5-dimethyl-2-oxo-2-cyclohexylamino-1,3,2-dioxaphosphorinane, v_{NH} is 3200 cm^{-1}.

[25] R. H. Iwamoto, E. M. Acton, L. Goodman and B. R. Baker, *J. Org. Chem.* **26**, 4743 (1961).

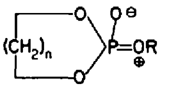
[26] K. Nakanishi, *Infrared Absorption Spectroscopy*. Holden-Day, San Francisco (1962).

The 3000 to 2000 cm^{-1} *region.* In common with other compounds possessing the arrangement X(:O)OH, where X is P, As, S, or Se,[27] the cyclic phosphoric acid exhibits three broad and rather ill-defined bands at 2550 to 2800, 2500 to 2100 and 1900 to 1700 cm^{-1}. These bands are not present in the spectra of esters of this acid, nor in the spectrum of its potassium salt and are attributable to vibrations of OH groups. The last band is at a slightly lower frequency than normally found for acyclic phosphorus acids.

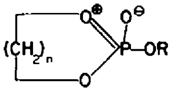
The SH stretching absorption for 5,5-dimethyl-2-thiono-2-thiolo-1,3,2-dioxaphosphorinane is found as a sharp band of medium intensity at 2548 cm^{-1} shifted to 2595 cm^{-1} in carbon tetrachloride solution. This is in agreement with that found for very dilute solutions of OO-dimethyl- and OO-diethyl- phosphorodithioic acids in the same solvent.[28] The latter acids in the pure form, and also as more concentrated carbon tetrachloride solutions, showed a broad band centred at around 2440 cm^{-1} and ascribed to S—H. . .S bonding. Similar absorption has also been noticed by the same authors[29] for the thiol group in some phosphorotetrathioic acids (MeS) (RS)P (:S) SH, and by Allen and Colclough[30] for diphenyl- and diethyl- phosphinodithioic acids. The broad bands in the range 2800 to 1700 cm^{-1} characteristic of the cyclic phosphoric acid, were absent from the spectrum of the cyclic dithio acid.[31]

In the case of compounds No. 1 and No. 13, bands at 2840 and 2820 cm^{-1} are suggested as being due to O-methyl and to N-methyl groups respectively.[26] The remaining bands within the range 3000 to 2850 cm^{-1} are to be found in all the compounds examined, and are assigned largely to CH_2 and CH_3 groups present in the ring.

The 1600 *to* 1000 cm^{-1} *region.* Owing to the spacial arrangement of the four bonds around the quinquivalent phosphorus atom, mesomeric effects involving the phosphoryl group and both endo and exo-cyclic bonds giving rise to structures such as VI and VII are weak since the system around the central phosphorus atom cannot become coplanar.[32] We may therefore disregard contributions from such structures when we are considering the effect of exocyclic groups on the absorption frequency of the phosphoryl group.



VI



VII

Jones and Katritzky[13] examined 2-oxo-2-ethoxy-1,3,2-dioxaphosphorinane (III; X = 0, R = OEt) and the corresponding dioxaphospholane (five-membered ring) and found phosphoryl absorptions at 1290 and 1287 cm^{-1} (in chloroform) respectively, compared with 1261 cm^{-1} for triethyl phosphate. A comparison of the spectra[33] of

---

[27] J. T. Braunholz, G. E. Hall, F. G. Mann and N. Sheppard, *J. Chem. Soc.* 868 (1959).

[28] A. Menefee, D. Alford and C. B. Scott, *J. Chem. Phys.* **25**, 370 (1956).

[29] D. Alford, A. Menefee and C. B. Scott, *Chem. & Ind.* 514 (1959).

[30] G. Allen and R. O. Colclough, *J. Chem. Soc.* 3912 (1957).

[31] The present preliminary study was restricted to the one solvent, and was further limited by the low solubility of the acid in that solvent (ca. 1%). Other solvents are to be included in a more detailed examination of this and other cyclic dithiophosphoric acids to be reported later.

[32] R. G. Gillis, J. F. Horwood and G. L. White, *J. Amer. Chem. Soc.* **80**, 2999 (1958).

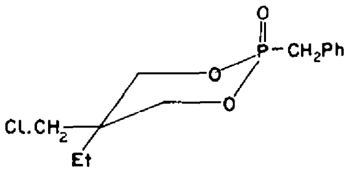
[33] J. R. Cox, jnr. and F. H. Westheimer, *J. Amer. Chem. Soc.* **80**, 5441 (1958).

2-oxo-2-benzyloxy-1,3,2-dioxaphospholane with the corresponding tervalent compound indicated bands at 1212 and 1300 cm^{-1} for the phosphate, absent from the spectrum of the phosphite. The phosphoryl absorption in 2-oxo-2-chloro-1,3,2-oxazaphosphorinane (V)[25] lies at 1274 cm^{-1}; replacement of the chlorine by a substituted amino group causes a lowering to 1206–1204 cm^{-1}.

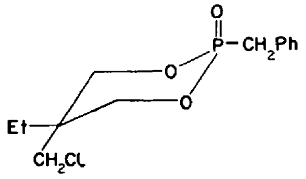
In the absence of any contributions from mesomeric structures, inductive effects appear to account largely for the relative positions of the phosphoryl absorptions. 2,5,5-Trimethyl-2-oxo-1,3,2-dioxaphosphorinane (II; X = 0, R = Me; $\nu_{P=O}$ 1260 cm^{-1}) may be considered as a standard for comparison purposes, since the inductive effect is here at a minimum, and there are no complicating side effects such as hydrogen bonding, as there would be in the case of the cyclic hydrogen phosphonate (II; X = 0, R = H).[4] The determined phosphoryl frequencies are then in the order predicted from a consideration of relative inductive effects. Thus, replacement of the methyl group by groups having a pronounced -I effect results in upward displacement of $\nu_{P=O}$ by 45 cm^{-1} (chloro-), 27–40 cm^{-1} (alkoxy-), 13–18 cm^{-1} (alkylthio-) and 22 cm^{-1} (dimethylamino-). In those cases where comparison between compounds with and without ring methyl groups is possible, effect of *gem*-dimethyl groups at position C-5 appears to be negligible. Monoalkylamino groups lower the value of $\nu_{P=O}$ by 17–31 cm^{-1} probably due to hydrogen bonding, with little variation due to size of the alkyl group. The N-t -butyl group (in compound 18) is notable in that it produces a system of strong bands in the region 1266 to 1228 cm^{-1}. Multiple bands at 1260–1230 cm^{-1} are also to be noticed for the phosphoramidates possessing the unsubstituted dioxaphosphorinane ring, the band of lower frequency corresponding to that for the C-5 dimethyl substituted compound.

In all the various groups of compounds examined, $\nu_{P=O}$ is seen to be at slightly higher values (10 to 30 cm^{-1}) than for the like acyclic compounds, the ranges for which are quoted by Thomas and Chittenden[34] who concluded that in the case of phosphoric esters this was the result of changes in the O—P—O angle. Alternatively, it could be due to smaller contributions from structures with $\overset{+}{P}$—$\overset{-}{O}$ in ring systems in which P=O is held more rigidly than in acyclic structures.

The problem of the conformation of phosphorus-containing rings is an interesting one, and one which is only now receiving attention. Wadsworth and Emmons[10] examined the reaction between 1-ethyl-4-phospha-3,5,8-trioxa-bicyclo(2,2,2)octane and benzyl chloride. One product only was formed, namely 5-chloromethyl-5-ethyl-2-oxo-2-benzyl-1,3,2-dioxaphosphorinane. Its conformation, (VIII) was predicted from the mode of preparation by a stereospecific Arbuzov reaction. It was produced together with the conformer (IX) by first a transesterification reaction between trimethyl phosphite and 2-chloromethyl-2-ethyl-propane-1,3-diol to yield 5-chloromethyl-5-ethyl-2-methoxy-1,3,2-dioxaphosphorinane, followed by reaction with



VIII



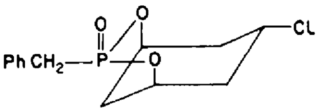
IX

---

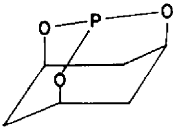
[34] L. C. Thomas and R. A. Chittenden (Miss), *Spectrochim. Acta* **20**, 467 (1964).

benzyl chloride. In both cases, P=O absorption frequencies were identical, namely 1260 cm^{-1}.

A bicyclic phosphonate has been examined by Berlin *et al.*[6,7] 3-Benzyl-3-oxo-7-chloro-2,4-dioxa-3-phosphabicyclo(3,3,1)nonane (X) was prepared from benzyl chloride and the bicyclic phosphite (XI). The boat-chair structure illustrated was the only tenable one, chair-chair and chair-boat structures being excluded on steric grounds. Here, equatorial P=O absorbed at 1257 cm^{-1}. This would appear to indicate that $\nu_{P=O}$ suffers little from conformational environment.

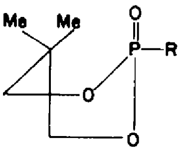


X

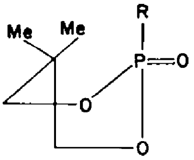


XI

Construction of models of the monocyclic phosphorus compounds under discussion suggests that the two possible boat conformations (XII and XIII) are unlikely because of repulsions between one of the C-5 methyl groups and either of the groups attached to the phosphorus atom.

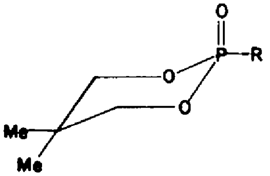


XII

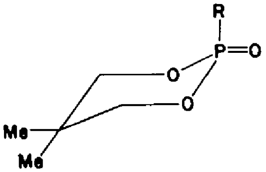


XIII

Of the two chair forms XIV and XV, the latter is the preferred one sterically, but XIV is not completely excluded particularly if R is relatively small, e.g. OMe, SMe, NMe$_2$. There is considerably more interaction if R is OEt, SEt, NHPr-i. The chair conformations seem even more likely in the 2-thiono series.

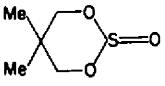


XIV

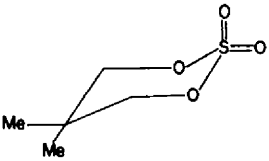


XV

At the moment it is only possible to predict the probability of a given conformation. It was hoped to aid this by a comparison of the spectra of the cyclic phosphorus compounds with those of 5,5-dimethyl-2-oxo-1,3,2-dioxathiane (XVI) and 5,5-dimethyl-2,2-dioxo-1,3,2-dioxathiane (XVII). The spectra of these two compounds are recorded in Table 3.



XVI



XVII

Because of steric interactions, the most probable structure of the cyclic sulphate is that shown, while the sulphite could exist with axial or equatorial S=O bond. A comparison of the spectra of 5-chloro-1,3,2-dioxathiane and the cyclic sulphite from 5-β-cholestane-3,5-diol led de la Mare *et al.*[35] to reason that in the first of these two compounds, the S=O group was equatorial. More recently, other workers[36] have produced evidence which would appear to contradict the earlier work. They were able to separate conformers of substituted 2-oxo-1,3,2-dioxathianes, and they concluded that axial and equatorial S=O groups absorbed at slightly different frequencies, namely 1190 and 1230 cm^{-1} respectively. Their conclusion was that in 5-chloro-2-oxo-1,3,2-dioxathiane, the S=O group is actually axial. The problem is therefore still not solved satisfactorily, and a comparison of the spectra of the ethyl phosphite and sulphite at this stage, is of doubtful value. A study of the NMR spectra of the phosphite (No. 2), phosphate (No. 7) and the cyclic sulphite and sulphate is at present being made, and the results will be published when available.

The possibility of distinguishing between cyclic and non-cyclic esters of phosphorus by means of measurements of P—O—C frequencies seems not to have been seriously considered. In a survey of such frequencies[37,38] for a number of acyclic phosphorus esters, Thomas and Chittenden suggest the range 900 to 1055 cm^{-1} for P^{v}—O—(C) stretching, and somewhat lower value for tervalent compounds. These are rather wider ranges than those quoted by Bellamy. All the cyclic compounds showed generally three distinct strong bands (Labelled A, B and C) within the range 950 to 1050 cm^{-1}. Thus the cyclic phosphites absorb at 1066–1055 (A), 1043–1035 (B) and 1016–1008 (C) cm^{-1}. The ranges for 5,5-dimethyl-2-oxo compounds are: 2-alkoxy, (A) 1077–1060, (B) 1046–1039, (C) 1012–1003 cm^{-1}; 2-alkylthio-, (A) 1057–1052, (B) absent, (C) 1005–1002 cm^{-1}; 2-alkylamino- (A) 1070–1054, (B) absent (C) 1015–1004 cm^{-1}. For the 5,5-dimethyl-2-thiono compounds the bands are at: 2-alkoxy (A) 1062–1056, (B) 1051–1038, (C) 1000–994 cm^{-1}; 2-alkylthio-, (A) 1049–1046, (B) absent (C) 992–994 cm^{-1}; 2-alkylamino-, (A) 1062–1054, (B) absent, (C) 1007–1000 cm^{-1}. In the case of the 2-thiono-2-alkylthio compounds, a band at 1049–1036 cm^{-1} which might have been considered as being band (B) for that series, could possibly be band (A) lower by the larger size of the alkylthio group. Similar groups of bands have also been observed in a number of 1,3,2-dioxaphospholanes. In 39 such compounds,[39] the overall range was again 1055 to 1000 cm^{-1} with the dithio compounds absorbing, in some cases, slightly below 1000 cm^{-1}. The three bands are not restricted to cyclic compounds, but they are to be found in the spectra of some acyclic compounds. Diethyl ethylphosphonate[32] has bands at 1049, 1027 and 1009 cm^{-1}. Other phosphonates, triethyl phosphite and triethyl phosphate do not possess the three-band system.[38] It is tentatively suggested that bands A and C are connected with phosphorus-oxygen ring vibration motions.

For nearly all the dioxaphosphorinanes examined, at least one weak to medium band is found around 1190 to 1150 cm^{-1} even in the absence of P—OEt and P—OMe

---

[35] P. B. D. de la Mare, W. Klyne, D. J. Millen, J. G. Pritchard and D. Watson, *J. Chem. Soc.* 1813 (1956).

[36] D. G. Hellier, J. G. Tillett, H. F. Van Woerden, R. F. M. White, *Chem & Ind.* 1956 (1963).

[37] L. C. Thomas and R. A. Chittenden (Miss), *Chem. & Ind.* 1913 (1961).

[38] L. C. Thomas and R. A. Chittenden (Miss), *Spectrochim. Acta.* **20**, 489 (1964).

[39] R. S. Edmundson and A. J. Lambie, unpublished results.

groups. Thus, the bands are not restricted to these arrangements, but more probably to P—O—C in general. A similar situation exists for the dioxaphospholanes[39] from ethanediol as well as from propane-1,2-diol, butane-2,3-diol and pinacol i.e. compounds containing methyl groups attached to ring carbon atoms. It was absent from unsubstituted dioxaphospholanes except when exocyclic P—OEt was present, and in the absence of this group can therefore be used to recognize ring substitution. With the exception of very few of the dioxaphosphorinanes reported here, all the compounds absorb in the overall range 1218 to 1200 cm^{-1} with variable intensity. The exceptions include the cyclic phosphoramidates from propane-1,3-diol and the cyclic phosphoric acid (compound No. 36). Aryloxy esters absorb strongly (not so the phenyl ester No. 38) here in addition to a band at slightly higher frequency normally associated with (P)—O—C (aryl) absorption.[23,26] The band may therefore be due to ring (P)—O—C vibrations in the absence of disturbances such as intermolecular hydrogen bonding of the type P(:O)OH. . . .O (ring) as is possible in the cyclic phosphoric acid.

The 1000 *to* 650 cm^{-1} *region.* Of importance here, are the P=S, P—N and P—O—C (aryl) vibrations. In addition, several workers have suggested that the region might be important in distinguishing between cyclic and acyclic structures.

It is widely recognized that absorption due to the thiophosphoryl group is more variable, both in intensity and in position, than the phosphoryl group, and it is probably less susceptible to movement by hydrogen bonding than the latter. Calculations[40] suggest that in $PSCl_3$, $\nu_{P=S}$ lies at 675 cm^{-1}, and indeed Hooge and Christen found that in a number of simple acyclic esters, the absorption lay at 685–580 cm^{-1}. If the compounds also contain P—N bonds, characterization becomes more difficult,[41,42] since this group also absorbs at around 700 cm^{-1}.

In 2-thiono-1,3,2-dioxaphospholanes,[39] it appears that $\nu_{P=S}$ is independent of the extent of ring substitution (one, two or four methyl groups). It does however depend on the nature of the exocyclic group attached to phosphorus. The following frequencies were assigned; 710–705 (exocyclic P—SEt), 680–660 (exocyclic P—NMe_2), and 690 cm^{-1} (exocyclic P—OEt). A number of insecticide analogues[19] based on the 5,5-dimethyl-2-thiono-1,3,2-dioxaphosphorinane system absorbed at 715 to 680 cm^{-1}. In the dioxaphosphorinanes now examined, comparison of the spectra of the 2-thiono esters with those of the corresponding tervalent esters indicates a strong band at 660–650 cm^{-1} assigned therefore to the P=S stretching frequency. In 2-alkylthio-1,3,2-dioxaphosphorinanes, the frequency rises to 690–680 cm^{-1}. It is more difficult to assign bands for the amino compounds due to their profusion for both phosphoramidates and phosphoramidothionates particularly since the former already possess a band at around 600 cm^{-1}. In both series, bands around 800 cm^{-1} are very variable, but that at 651 ± 9 cm^{-1} is assigned to P=S in the phosphoramidothionates. In addition, with the exception of the dithio acid, the cyclic phosphorochloridothionate, and the methoxy and propoxy esters, all the 2-thiono compounds possess a band of variable intensity at 810–800 cm^{-1} which according to Chittenden and Thomas[42] may be linked with P=S absorption, two bands falling in the overall ranges 862–685 and 730–550 cm^{-1} always being present when the P=S arrangement occurs. On the other

---

[40] F. N. Hooge and P. J. Christen, *Rec. Trav. Chim.* 77, 911 (1958).

[41] R. A. McIvor, G. A. Grant and C. E. Hubley, *Canad. J. Chem.* 34, 1611 (1956).

[42] R. A. Chittenden (Miss) and L. C. Thomas, *Spectrochim. Acta*, in press.

hand, it is equally likely that the higher frequency band is the equivalent of that at approximately 820 cm^{-1} found for many of the 2-oxo compounds, substituted and unsubstituted at C_6, but absent from the spectra of the phosphites.

Comparison of the spectra of the phosphoramidothionates with the other thiophosphoryl compounds suggests that a band of moderate to very weak intensity at 778 to 727 cm^{-1} could well be connected with the P—N bond. Thomas and Chittenden[37] feel that no direct correlations are possible for this bond, but simplified calculations show that absorption should occur at around 780 cm^{-1}. The wide variation in the position of the band may be the result of differences in physical state, but more likely, mass effects, considered to be of particular importance in connection with this bond (Ref. 23, page 323). For the phosphoramidates a greater number of bands is apparent, and the general trend is to higher frequencies, with one or both bands within the range 790 to 725 cm^{-1} assigned to P—N.

The spectra of aryloxy-dioxaphosphorinanes show strong bands at around 930 cm^{-1} in agreement with the range quoted by Chapman and Harper[43] and by Thomas and Chittenden[38] for quinquivalent phosphorus compounds. Direct P—C(aryl) bonds produce no such strong absorption.

All the compounds examined in this study, display a large number of bands of various intensities in the 950 to 650 cm^{-1} range, which have not already been allocated to the groups so far discussed, and a few appear to be common to all compounds irrespective of the substituent at position 2. They occur at ca. 990 (m-s), 915–920 (m), ca. 950 (m), ca. 790 (w-s) and at ca. 770 cm^{-1} (vw-m). The claims by Cason, Baxter and DeAcetis[12] that five- and six-membered rings may be distinguished by the bands which occur at 924–922 and 936–934 cm^{-1} respectively, have been criticized by Jones and Katritzky[13] who examined cyclic ethyl phosphites and phosphates from ethylene and trimethylene glycols. Burgada[11] observed a band at 920 cm^{-1} for 2-N-dimethylamino-1,3,2-dioxaphospholane, and at 910 cm^{-1} for 2-ethoxy-1,3,2-dioxaphospholane, but no such band for the corresponding 2-t-butoxy ester. Moreover, a large number of other 1,3,2-dioxaphospholanes[39] absorb at around 945–915 and 795–755 cm^{-1}, many of them also at 970 cm^{-1}. It is felt therefore that the 1000 to 750 cm^{-1} region is of little value to distinguish between ring sizes and cyclic and acyclic structures.

Acknowledgement—Dr. A. J. Lambie and the staff of the Microanalytical Laboratory, Fisons Pest Control Limited, Cambridge, are thanked for analyses.

---

[43] A. C. Chapman and R. Harper, *Chem. & Ind.* 985 (1962).