849. *Infrared and Nuclear Magnetic Resonance Spectra of Some Cyclic Phosphorus Compounds.*

By Richard A. Y. Jones and A. R. Katritzky.

The nuclear magnetic resonance of phosphorus atoms in cyclic compounds could not be simply correlated with ring size. The frequency variation of the P=O stretching mode in cyclic phosphates does not parallel that of the C=O mode of lactones.

Cyclic phosphates are of importance in biological systems, for example as intermediates in the hydrolysis of RNA[1] and of phospholipids,[2] and commercially in insecticides and plasticisers.

Salts of ethylene hydrogen phosphate (I; $R = O^-M^+$) undergo alkaline hydrolysis *ca.* 10^7 times more rapidly than salts of dimethyl hydrogen phosphate.[2a] Ethylene methyl phosphate (I; R = OMe) is hydrolysed by alkali *ca.* 2×10^6 times as rapidly as trimethyl phosphate, and heats of hydrolysis indicate that the cyclic ester is the less stable by 7—9 kcal.[3] Westheimer has suggested that strain in the five-membered ring of cyclic phosphates accounts for these results, and points out that this strain should be relieved in six-membered ring phosphates;[4] these compounds are apparently hydrolysed much less quickly (cf. ref. 4).

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[1] Brown and Todd, *Ann. Rev. Biochem.*, 1955, **24**, 311.

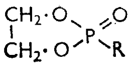
[2] Dawson, *Ann. Rep.*, 1958, **55**, 365.

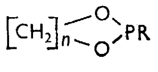
[2a] Kumamoto, Cox, and Westheimer, *J. Amer. Chem. Soc.*, 1956, **78**, 4858,

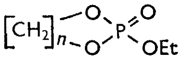
[3] Cox, Wall, and Westheimer, *Chem. and Ind.*, 1959, 929.

[4] Westheimer, *Chem. Soc. Spec. Publ. No.* 8, 1957, p. 1.

The present work was carried out to determine whether the ring size of cyclic phosphorus compounds could be correlated with spectral characteristics. The phosphorochloridite (II; R = Cl), phosphite (II; R = OEt), and phosphate (III) with five- and


(I)


(II)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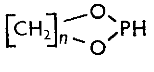
(IV)

six-membered rings (n = 2 or 3) were studied and compared with diethyl phosphorochloridite, triethyl phosphite, and triethyl phosphate.

Nuclear magnetic resonance peaks, measured as p.p.m. relative to 85% phosphoric acid, were:

	Phosphorochloridite	Phosphite	Phosphate
Five-ring	−167	−131	−17
Six-ring	−153	−128	+7
Acyclic	−164	−138 ± 1 *	+1 ± 1 *

* Ref. 5.

The resonance peaks for the six-membered rings are at 6—11 p.p.m. to higher fields than for the acyclic analogues. The effect of a five-membered ring can cause shifts to either higher or lower field values. Thus there is no simple relation between ring size and the position of peak. Van Wazer and co-workers[6] reported *ca.* −160 p.p.m. for diphenyl phosphorochloridite.

The infrared spectra of 0·185M-chloroform solutions were measured in a 0·108 mm. cell, and apparent extinction coefficients were recorded (for the errors and approximations involved therein see ref. 7). The νP=O band was found at 1290 cm.$^{-1}$ (400),[†] 1287 (400), and 1261 (380), for the six- and five-membered rings and the acyclic compound, respectively. This behaviour differs from that of νC=O in cyclic carbonyl compounds where six-membered rings and acyclic compounds absorb at comparable frequencies but five-membered ring compounds some 40 cm.$^{-1}$ higher. Thus there is no correlation with hydrolysis rates.

In this region, the phosphites showed weak bands at *ca.* 1290 cm.$^{-1}$ (20) and the cyclic phosphorochloridites moderate ones at 1277 (75) and 1289 (90), of unknown origin.

Reasonable assignments can be suggested for the remaining bands of the cyclic compounds with $\varepsilon_A > 10$. A ring CH deformation mode was found at 1480—1474 cm.$^{-1}$ (15—35) for the five-membered rings. Dioxolans show the CH_2 scissor mode of the $[CH_2]_2$ group at 1480 cm.$^{-1}$ (cf. ref. 8*a*). For the six-membered rings seven bands were found at 1483—1477 (30—40), 1470—1465 (25—30), 1433—1429 (25—30), 1374—1371 (20—40), 1142—1136 (70—160), 890—888 (50—85), and 874—861 (85—210). The infrared spectrum of trimethylene sulphite[8b] shows bands at 1467 m, 1428 s, 1367 m, 1141 w, 904 w, 855 s, which correspond closely to all but the first of the sequence listed above.

Bands characteristic of the ethyl group for the cyclic phosphites and phosphates were found:

1448—1445	(25—30)	methyl asym. bend	1442 ± 2	(25 ± 5)
1398—1391	(30—50)	methyl sym. bend	1392 ± 3	(60 ± 20)
1165—1161	(25—45)	methyl rock (in-plane)	1113 ± 2	(55 ± 10)
1095—1092 *	(45—50)	methyl rock (out-of-plane)	1089 ± 2	(25 ± 5)

[†] The following conventions are used: parentheses enclose apparent maximum extinction coefficients calculated by using the equation $\varepsilon_A = (1/Cl) \log_{10} (I_0/I)$. * denotes shoulder.

[5] Mean values from (*a*) Muller, Lauterbur, and Goldenson, *J. Amer. Chem. Soc.*, 1956, **78**, 3557; (*b*) Callis, Van Wazer, Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, 1956, **78**, 5715; (*c*) Finegold, *Ann. New York Academy*, 1958, **70**, 875.

[6] Fluck, Van Wazer, Groenweghe, *J. Amer. Chem. Soc.*, 1959, **81**, 6363.

[7] Katritzky, Monro, Beard, Dearnaley, and Earl, *J.*, 1958, 2182.

[8] (*a*) Barker, Bourne, Pinkard, and Whiffen, *J.*, 1959, 802; (*b*) de la Mare, Klyne, Millen, Pritchard, and Watson, *J.*, 1956, 1813.

[9] Mortimer, *Spectrochim. Acta*, 1957, **9**, 270.

These assignments are based on those for the ethyl vibrations in ethyl ethers,[10] for which the arithmetical means and standard deviations are given in the right-hand column. The methylene and ring scissor bands are apparently superimposed near 1480 cm.^{-1}. The methylene wagging mode is found solely for the cyclic phosphates at 1374—1371 cm.^{-1} (40—50), this mode is known to be very sensitive to the environment of the ethyl group.[7,10] Three bands have been reported [11] for the Et–O–P group near 1480, 1445, and 1395 cm.^{-1}, and a fourth band at *ca.* 1370 cm.^{-1} was found for compounds containing the grouping Et–O–P(=O). Other bands at 1168—1160 cm.^{-1} and *ca.* 1105 cm.^{-1} were previously assigned to C–O and P–O modes. Precise intensities have not been reported before.

P–O and C–O stretching modes cause bands in the 1100—1000 cm.^{-1} region. Absorption for the phosphates is similar for all three compounds:

Six-ring	1073 (380)	1034 (1000)	968 (400)
Five-ring	1060 * (210)	1032 (1000)	975 (120)
Acyclic	1070 * (175)	1032 (1200)	976 (400)

Ranges 1036—1029 and 990—971 cm.^{-1} have previously been given for bands of these types in phosphates.[11] Corresponding absorption for the other classes of compounds depends more on the ring size:

	Phosphite		Phosphorochloridite		
Six-ring	1066 (420)	1041 (460)	1062 (480)	1020 * (50)	
Five-ring	1045 (210)	1011 (330)	1049 (70)	1028 * (75)	1008 (410)
Acyclic	1021 (1000)	979 * (65)	1075 * (65)	1015 (460)	

Bands characteristic of the 1,3,2-dioxaphospholane (IV; $n = 2$) and -dioxaphosphorinane (IV; $n = 3$) rings have been reported [12] at 924—922 and 936—934 cm.^{-1}, respectively, and it was stated that such bands have not been observed in any other phosphorus compounds. In the 950—900 cm.^{-1} region the compounds now investigated showed the following bands:

	Phosphate	Phosphite		Phosphorochloridite		
Six-ring	930 (190)	929 (290)		953 * (70)	934 (280)	
Five-ring	926 (135)	911 (220)		922 (180)		
Acyclic	—	935 * (180)	910 (480)	974 (160)	957 (170)	928 (170)

Obviously Cason, Baxter, and De Acetis's [12] correlations must be used with caution. A band at *ca.* 917 cm.^{-1} has been suggested as characteristic of the group P–OEt.[11]

EXPERIMENTAL

All compounds were redistilled immediately before measurement.

Measurement of Spectra.—For conditions of measurement, etc., of infrared spectra see refs. 7 and 13. Nuclear magnetic resonance spectra were obtained at 16·2 Mc./sec. with a Varian Associates 4300 B spectrometer and 12 in. electromagnet with flux stabilisation and non-spinning 10-mm. sample. 85% Orthophosphoric acid was used as an external standard for phosphorus(V) measurements and trimethyl phosphite for phosphorus(III). For conversion, trimethyl phosphite was taken as having a chemical shift of -139 p.p.m. relative to orthophosphoric acid.[5c]

Ethylene and trimethylene phosphorochloridites and phosphites were prepared by the method of Lucas, Mitchell, and Scully,[14] and redistilled 3—5 times. Satisfactory carbon and hydrogen analyses were obtained for all the compounds and their refractive indexes and boiling points agreed with those previously reported,[14] although some compounds were prone to super-heating.

Cyclic phosphates were prepared by oxidising the appropriate phosphites in dichloromethane with a dichloromethane solution of dinitrogen tetroxide at $-80°$.[15] *Ethyl ethylene phosphate* had b. p. $62°/10^{-2}$ mm., n_D^{20} 1·4271 (Found: C, 31·3; H, 6·1. $C_4H_9O_4P$ requires C, 31·6;

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[10] Katritzky and Coats, *J.*, 1959, 2062.
[11] McIvor, Grant, and Hubley, *Canad. J. Chem.*, 1956, **34**, 1611.
[12] Cason, Baxter, and DeAcetis, *J. Org. Chem.*, 1959, **24**, 247.
[13] Katritzky and Lagowski, *J.*, 1958, 4155.
[14] Lucas, Mitchell, and Scully, *J. Amer. Chem. Soc.*, 1950, **72**, 5491.
[15] Cox and Westheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5441.

H, 6·0%). *Ethyl trimethylene phosphate* had b. p. 77—79°/10^{-2} mm., n_D^{20} 1·4386 (Found: C, 36·0; H, 6·7. $C_5H_{11}O_4P$ requires C, 36·15; H, 6·7%).

Diethyl phosphorochloridite, prepared by Saunders and his co-workers' method,[16] had b. p. 38—39°/12 mm., n_D^{20} 1·4377 (lit. b. p. 34—42°/13 mm.).

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[16] Cook, Ilett, Saunders, Stacey, Watson, Wilding, and Woodcock, *J.*, 1949, 2921.