reflections of each of five general reflections. Least squares calculations gave the following lattice parameters: $a = 6.913(0.007)$ Å; $b = 21.116(0.004)$ Å; $c = 5.829(0.006)$ Å.

Figures in parentheses are estimated standard deviations.

The density of the crystals was measured by flotation to be 1.41 g cm^{-1}. The calculated density with *four* molecules per unit cell is 1.414 g cm^{-1}.

Khawas and Krishna Murti [1] concluded with a unit cell twice as large, the a-axis being 13.89 Å and b and c 21.08 Å and 5.84_2 Å, respectively.

Intensity data have been collected with the use of an automatic Picker diffractometer. The crystal structure is presently being investigated using 2259 reflections observed above the background level.

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Acid Strengths of Mononaphthyl Phosphates

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In connection with studies of reactions of several phosphoric acids and esters in this laboratory, the values of the second dissociation constants of mononaphthyl phosphates ($C_{10}H_7OPO_3H_2$) in aqueous potassium chloride solutions were determined potentiometrically. Both of these esters of orthophosphoric acid, 1-naphthyl phosphate and 2-naphthyl phosphate, are of interest in biochemical research and as analytical reagents.

The pK_2 values 5.848 ± 0.005 and 5.762 ± 0.003 were obtained for the dissociation constants of 1-naphthyl and 2-naphthyl phosphates, respectively, at ionic strength 0.1 and 25°C. These values were evaluated by fitting the Debye-Hückel equation

$$pK_2 = pK_2^0 - 2.036\sqrt{I}/(1+\alpha\sqrt{I}) + B\,I$$

to experimental data obtained at various ionic strengths (0 – 2.0 M KCl).

Table 1. Values of the second dissociation constants of mononaphthyl phosphates in aqueous solution at 25°C. Titrant 0.1 M NaOH.

	c_B:c	pH	$\sqrt{I}$	pK_2
1-Naphthyl phosphate	0.280	5.695	0.105	6.064
$c = 4.002 \times 10^{-3}$ M	0.337	5.810	0.107	6.061
$pf_{H^+} = 0.044$	0.390	5.910	0.109	6.062
	0.445	6.010	0.111	6.064
	0.500	6.106	0.113	6.062
	0.555	6.199	0.114	6.060
	0.610	6.300	0.116	6.061
	0.665	6.401	0.118	6.058
	0.720	6.516	0.119	6.060
2-Naphthyl phosphate	0.279	5.617	0.108	5.986
$c = 4.190 \times 10^{-3}$ M	0.339	5.741	0.110	5.988
$pf_{H^+} = 0.045$	0.399	5.852	0.112	5.987
	0.430	5.906	0.113	5.985
	0.489	6.016	0.115	5.990
	0.520	6.067	0.116	5.987
	0.590	6.190	0.118	5.987
	0.652	6.303	0.120	5.985
	0.714	6.430	0.122	5.987

Illustrative titration data are shown in Table 1. The computed values of the thermodynamic constants and the parameters of the Debye-Hückel equations are listed in Table 2.

The mononaphthyl phosphates are clearly stronger acids than orthophosphoric acid itself. The 2-naphthyl ester seems also to

Table 2. pK_2 values of mononaphthyl phosphates at 25°C.

	I	pK_2	α	B
1-Naphthyl phosphate	Zero	6.27	1.51	0.10
	0.1	5.85		
	1.0	5.57		
2-Naphthyl phosphate	Zero	6.19	1.52	0.10
	0.1	5.76		
	1.0	5.48		

be a slightly stronger acid than the 1-naphthyl ester, which is also the order of acid strengths of the naphthyl esters of other inorganic oxyacids. 2-Naphthol itself is, however, a weaker acid than 1-naphthol.[1]

In connection with their studies on the hydrolysis of several organic phosphates, Chanley and Feageson reported the pK_2 values 5.85 and 5.83 for 1-naphthyl and 2-naphthyl phosphates, respectively, at 26 ± 1°C and at ionic strength 0.1.[2] Our value is thus exactly the same for 1-naphthyl phosphate, but our value for 2-naphthyl phosphate differs somewhat from the value of Chanley and Feageson. The pK_1 values 0.97 and 1.28 are also reported,[2] for 1-naphthyl and 2-naphthyl phosphate, respectively.

The pK_2^0 value 6.28 (25°C, $\alpha = 1.41$, $B = 0.15$) for monophenyl phosphate ($C_6H_5OPO_3H_2$) may be noted for comparison.[3]

Experimental. 1-Naphthyl phosphate from Aldrich Chemicals Co., disodium 1-naphthyl phosphate dihydrate from British Drug Houses Ltd., and disodium 2-naphthyl phosphate dihydrate from Aldrich Chemicals Co. were used when purified by recrystallization from water. The experimental methods and apparatus have been described earlier.[3] The hydrogen ion concentrations were calculated with the aid of hydrogen ion activity coefficient values.[4]

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Geometric Isomers of 3-Methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinane

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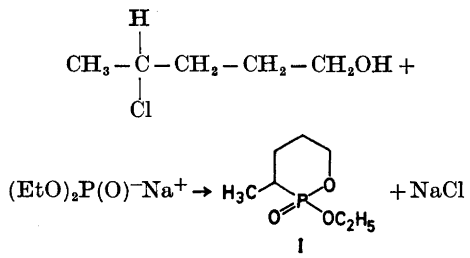
Some time ago the isolation of *cis* and *trans* isomers of 5-methyl- and 6-methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinanes was reported.[1] They were prepared upon heating triethylphosphite with 2-methyl-1,4-dibromobutane or 1,4-dibromopentane, respectively.

This paper reports the preparation of the geometric isomers of 3-methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinane (I). The isomeric mixture was prepared from sodium diethylphosphite and 4-chloropentanol according to the method of Songstad.[2]



Compound I was found by gas liquid chromatography (GLC) to contain the geometric isomers in the ratio approx. 1:1. The isomers were separated by preparative GLC, and the *cis* isomer is believed to be the isomer with the shortest retention time. Physical data as refractive index, retention time, P=O frequency, chemical shifts, and coupling constants of the isomers are given in Table 1.

Table 1. Physical data, chemical shifts and coupling constants for the *cis* and *trans* isomers of I.

Isomer	Retention time (min) 175°	n_D^{20}	$\nu_{P=O}$ cm^{-1}	δCH_3 chemical shift, ppm	Coupling constants Hz
cis	20	1.4525	1230	1.11	$J_{H-CH_3} = 6.3$, $J_{P-C-CH_3} = 17.6$
trans	30	1.4483	1230	1.16	$J_{H-CH_3} = 6.3$, $J_{P-C-CH_3} = 22.1$