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]

1. Mäkitie, O. *Suomen Kemistilehti* **B 39** (1966) 23.
2. Chanley, J. D. and Feageson, E. *J. Am. Chem. Soc.* **77** (1955) 4002.
3. Mäkitie, O. and Konttinen, V. *Acta Chem. Scand.* **23** (1969) 1459.
4. Näsänen, R., Lumme, P. and Mukula, A.-L. *Acta Chem. Scand.* **5** (1951) 1199.

Received March 3, 1971.

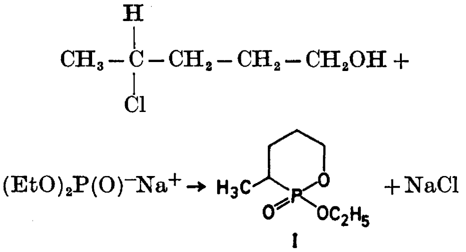
Geometric Isomers of 3-Methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinane

KNUT BERGESEN and TROND VIKANE

Chemical Institute, University of Bergen, N-5000 Bergen, Norway

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]



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-CH_2-CH_2-CH_2OH +$$

I

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.

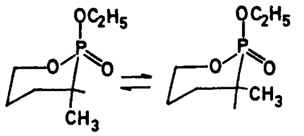
Isomer	Retention time (min) 175°	n_D^{20}	$\nu_{P=O}$ cm^{-1}	δCH_3 chemical shift, ppm	Coupling constants Hz
cis	20	1.4525	1230	1.11	$J_{H-CH_3} = 6.3$, $J_{P-C-CH_3} = 17.6$
trans	30	1.4483	1230	1.16	$J_{H-CH_3} = 6.3$, $J_{P-C-CH_3} = 22.1$

Rigidity of the phosphorinane rings is indicated by the PMR spectra of the isomers which showed no change over the temperature range −90° to +140°.

Infrared spectra of different *cis* and *trans* isomers of dialkylcyclohexanes [3] reveal characteristic frequencies in the region 585−650 cm^{-1} only for those isomers having at least one axial substituent. In the 1.2 series, the frequency range was 585−605 cm^{-1}. No characteristic frequency was observed for the equatorial substituted isomers in the region 560−770 cm^{-1}. The infrared spectrum of the *cis* isomer of I showed three strong bands at 559, 600 and 689 cm^{-1}, and the *trans* isomer two bands at 555 and 679 cm^{-1}. The appearance of the band at 600 cm^{-1} in the *cis* isomer is assigned to an axial substituted methyl group at carbon 3, and the lack of this band in the *trans* isomer indicates an equatorial methyl group. The infrared spectra of the two isomers show no differences between the phosphoryl absorption bands (Table 1), indicating the same $P=O$ configuration around the phosphorus atom in both isomers.

The PMR of the 3-methyl group in the *cis* and *trans* isomers consist of two doublets due to the coupling to the methine proton as well as to the phosphorus atom. The chemical shifts for the 3-methyl group in the isomers were slightly different, and the methyl phosphorus coupling, $^3J_{P-C-CH_3}$, is found to be 17.6 and 22.1 Hz, respectively.

Molecular models point to an equatorial position of the phosphoryl oxygen group in both isomers. This is also supported by the structures of corresponding phosphorinane compounds.[7–9] Some steric repulsion between the axial methyl group at carbon 3 and axial hydrogen at carbon 5 in I is expected, but repulsion may also be expected between the equatorial methyl group in 3 position and the freely rotating axial ethoxy group linked to phosphorus. These steric repulsions are assumed to be of similar magnitude. The equatorial position of the methyl group at carbon 3 probably causes a greater distortion of the chair conformation as compared to a methyl group in an axial position. This probably results in a larger P−C−C−H dihedral angle and a greater methyl phosphorus coupling as compared to the isomer with axial methyl group. According to these arguments it is reasonable to assume the following structures for the *cis* and *trans* isomers of I:



cis *trans*

The proposed structures agree with the modified Auwers-Skita rule [4,5] and the relative retention time [6] according to which the *cis* isomers of 1,2-disubstituted cyclohexanes have higher refractive indexes and shorter retention time on a gas-chromatographic column (Table 1). The conformational equilibria of the *cis* and *trans* isomers of I have also been studied at 5 different temperatures over a range of approx. 100°C. The equilibrations were carried out in sealed tubes and catalyzed by trifluoroacetic acid; each sample was analyzed by GLC. The equilibrium was approached from both sides, or from the mixed isomers. The conformational equilibrium constant was found in every case to be nearly 1, indicating identical stability of the *cis* and *trans* isomers; *i.e.* the enthalpy of isomerization, ΔH, is about zero.

Further detailed studies and analysis of proton magnetic resonance spectra of the isomers is in progress in this laboratory.

Experimental. 3-Methyl-2-oxo-2-ethoxy-1,2-oxaphosphorinane (I) was prepared from 23.2 g (0.14 mol) sodium diethylphosphite and 16.3 g (0.13 mol) 4-chloro-1-pentanol according to the method of Songstad.[2] The isomeric mixture was fractionated *in vacuo* in a heated jacket column to give 3.4 g (15 %) b.p.$_1$ 108°, n_D^{20}: 1.4500. GLC purity of I>90 %. The isomers were separated by means of an Aerograph Autoprep A-700 gaschromatograph. GLC purity of the isomers was above 99 %. The PMR spectra were measured at 60 MC (JEOL−60H) in neat liquid at 25°C, in 20 % solution of the isomers in CCl_4 at 140°C, and 20 % solution of the isomers in dichloromethane at −90°C. The infrared spectra below 700 cm^{-1} were recorded on a Unicam SP 100 instrument, from samples prepared as films between KBr-windows.

1. Bergesen, K. *Acta Chem. Scand.* **21** (1967) 578.
2. Songstad, J. *Acta Chem. Scand.* **21** (1967) 1681.
3. Zhizhin, G. N., Stein, Kh. E., Aleksanyan, V. T. and Lieberman, A. L. *Zh. Strukt. Khim.* **6** (1965) 684.

4. von Auwers, K. *Ann.* **420** (1920) 84.
5. Skita, A. *Ber.* **56** (1923) 1014.
6. Eliel, E. L. *Stereochemistry of Carbon Compounds*, McGraw, New York 1962, p. 217.
7. Beineke, T. A. *Chem. Commun.* **1966** 860.
8. Geise, H. J. *Rec. Trav. Chim.* **86** (1967) 362.
9. Muragaa, W. and Kainosko, M. *To be published in Bull Chem. Soc. Japan.*

Received February 23, 1971.

Mean Amplitudes of Vibration for Tetrakis(trifluorophosphine)-nickel

S. J. CYVIN [a] **and A. MÜLLER** [b]

[a] ***Institutt for teoretisk kjemi, Norges tekniske høgskole, N-7034 Trondheim, Norway and***
[b] ***Institut für Chemie, Universität Dortmund, West-Germany***

Tetrakis(trifluorophosphine)nickel, $Ni(PF_3)_4$, has recently been subjected to two independent gas electron diffraction works.[1,2] The results from these works agree well for the interatomic distances, but there is a controversy as regard to the P···P mean amplitude. Marriott *et al.*[1] have reported 0.2 – 0.3 Å in consistence with a rough estimate of 0.2 Å from spectroscopic data, while Almenningen *et al.*[2] have given $u(P \cdots P) = 0.101$ (0.016) Å. In the present work it is attempted to give a more accurate answer to this problem from elaborate spectroscopic calculations.

A diagonal force constant matrix in terms of symmetry coordinates[3] was chosen as the initial approximate form. After some preliminary calculations the following values of force constants were accepted as a starting point. Species A_1: 3.28, 8.08, and 0.86 mdyne/Å. A_2: 0.0294 mdyne/Å. E: 0.079, 4.164, 0.386, and 0.5 mdyne/Å. F_1: 4.50, 0.40, 0.40, and 0.0294 mdyne/Å. F_2: 2.27, 0.06, 5.25, 5.50, 0.55, 0.58, and 0.40 mdyne/Å. The calculated frequencies from this force field are shown in Table 1 along with available experimental data.[4-6]

Table 1. Vibrational frequencies (cm^{-1}) for tetrakis(trifluorophosphine)nickel

Species	Raman (liquid) a	Raman (liquid) b	Infrared (gas) a	Infrared (gas) b	Calculated c	Calculated d
A_1	954	955	—	—	972	954
	534	534	—	—	518	534
	195	195	—	—	198	195
A_2	63?	—	—	—	63	63
E	851	—	—	—	865	851
	332	—	—	—	339	332
	—	—	—	—	301	301
	54	—	—	—	54	54
F_1	—	—	—	—	890	890
	—	—	—	—	349	349
	—	—	—	—	271	271
	—	—	—	—	37	37
F_2	883	892	898	894	968	898
	883	850	860	857	809	860
	505	501	508	—	528	508
	385	383	390	—	403	390
	—	—	287?	—	261	287
	219	218	217	—	216	217
	54	50	52	—	52	52

a. Refs. 3 and 4.
b. Ref. 5.
c. From initial approximate force field.
d. From final force field.

The calculated mean amplitudes from the approximate force field are given as parenthesized figures in Table 2. The calculations were refined by adjusting the force constants to the frequency values shown in the last column of Table 1, where observed values have been used when available. The spectral data are seen to be rather incomplete, for which reason the final mean amplitudes (Table 2) must not be accepted without criticism. In particular the torsional frequencies of species A_2 and F_1 (lowest frequency) are very uncertain. The mean amplitudes which are substantially influenced by the values of these frequencies are marked in the table.

In spite of the large uncertainties of the present calculations the P···P mean amplitude seems to be fairly well established. Its value at room temperature appears to be in-between the two different estimates from electron diffraction, but the drastic dependence on temperature should be noticed. In general the electron