SHORT COMMUNICATIONS

Conformational Dependence of P=O Stretching Vibration Frequency in Six-membered Cyclic Phosphates

Masatsune KAINOSHO, Toshikatsu MOROFUSHI and Asao NAKAMURA

Central Research Laboratories, Ajinomoto Co., Inc., Suzuki-cho, Kawasaki

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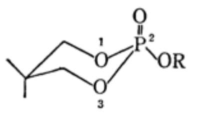
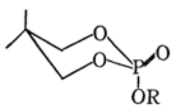
It has been reported that the P=O stretching frequency ($\nu_{P=O}$) does not show any appreciable dependency on the conformational environments of 1,3,2-dioxaphosphorinane system,[1,2] although the $\nu_{S=O}$ in six-membered cyclic sulfites is quite sensitive to the conformations.[3] NMR and dipole moment studies[4] have shown that the P=O bond is mainly at the equatorial rather than the axial position. The same conformation is also confirmed by the X-ray diffraction method[5] in the crystalline state of several phosphates.

In this communication we wish to present the unequivocal evidence of conformational dependence of $\nu_{P=O}$, which is contrary to previous reports. The infrared spectra of 5,5-dimethyl-2-oxo-2-alkoxy-(or 2-aryloxy)-1,3,2-dioxaphosphorinanes were carefully examined both in solid phase (KBr tablet) and in carbon tetrachloride solution.



α



β

In solid phase, all of the compounds examined show a symmetrical single absorption at 1284—1305 cm^{-1} which can be assigned to $\nu_{P=O}$, but in solution an extra band at 1267—1298 cm^{-1} followed by the strong absorption at 1308—1322 cm^{-1} (see Table 1). These bands are assignable to $\nu_{P=O}$ because they were shown to shift by the addtion of phenol possibly due to the formation of hydrogen bonding. The origin of this phenomenon (*i. e.* two $\nu_{P=O}$'s) is attributable to the conformational equilibrium, $\alpha \leftrightarrow \beta$. With I—V, the relative intensity of the higher frequency bands are much stronger than the lower ones, indicating that the former are equatorial and the latter are axial $\nu_{P=O}$. This assignment is compatible with the general trend that the axial stretching frequency is lower than the equatorial one.

TABLE 1.

Compound*	$\nu_{P=O}$ cm^{-1}		
	KBr	CCl$_4$ sol.	+Phenol
2-Methoxy- (I)	1287	1313 1272	1285 1234
2-Ethoxy- (II)	—**	1309 1267	1283 1230
2-Isopropoxy- (III)	1284	1308 1268	1277 1231
2-*p*-Anisyl- (IV)	1297	1322 1298	1294 1228
2-(3,5-Dimethyl)phenoxy- (V)	1305	1322 1294	1290 1228
2-(2,6-Dimethyl)phenoxy- (VI)	1304	1319 1287	1294 1227
2-(2,6-Di-*t*-butyl-4-methyl)-phenoxy- (VII)	1297	1314 1286	1288 1230

* Preparation of these compounds will be described elsewhere.

** Liquid at room temperature.

Clearer examples are supplied by VI and VII, in which β-conformation may be expected to have a strong 1,3-diaxial repulsion between the ring hydrogens and the substituents at aryloxy groups. Thus, the intensity ratios of two bands ($\nu_{P=O_{eq}}$: $\nu_{P=O_{ax}}$) are roughly estimated as 4 : 1 and 1 : 1 for VI and VII, respectively. These ratios are in agreement with the NMR results which will be published elsewhere.

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1) R. S. Edmundson, *Tetrahedron*, **20**, 2781 (1964).

2) R. A. Y. Jones and A. Y. Katritzky, *J. Chem. Soc.*, **1960**, 4376.

3) H. F. Van Woerden and E. Havinga, *Rec. Trav. Chim. Pays-Bas.*, **86**, 341 (1967).

4) M. Kainosho and T. Shimozawa, *Tetrahedron Letters*, in press.

5) W. Murayama and M. Kainosho, This Bulletin, in press, and references cited therein.