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DIPOLE MOMENT AND CONFORMATION OF THE 2,2-DISUBSTITUTED-1,3,2-DIOXAPHOSPHORINANES

M. Kainosho* and T. Shimozawa**

* Central Research Laboratories, Ajinomoto Co. Inc.
2964 Suzukicho, Kawasaki, Japan

** Department of Chemistry, Faculty of Science and Technology
Saitama University, Shimoohkubo, Saitama, Japan

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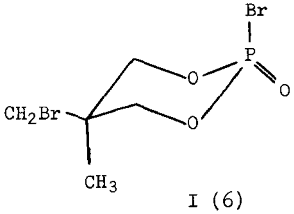
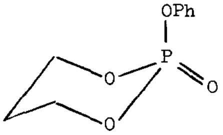
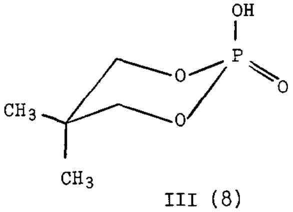
Recently, attention has been directed to the conformation of 2,2-disubstituted-1,3,2-dioxaphosphorinanes (1-5). The X-ray diffraction method has been applied to three compounds (I, II, III), and a chair-like structure carrying a P=O bond at an equatorial position has been confirmed.



I (6)



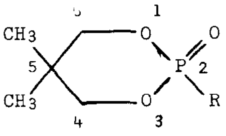
II (7)



III (8)

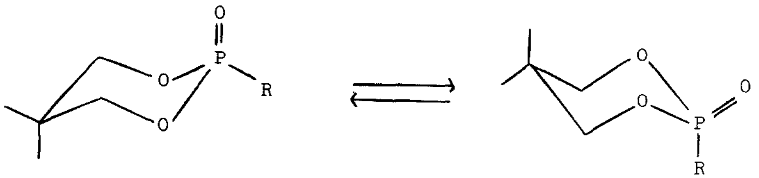
In solution, however, no such convincing evidence of the preferred conformation has been obtained as yet. By nmr technique, it has only been concluded that the 1,3,2-dioxaphosphorinane ring exists as a chair-like structure with either an axial or an equatorial P=O group (1).

In this letter, the preferred conformation of various six-membered phosphates and phosphoroamidates is advanced on the ground of their dipole moments. The dipole moments of the following seven compounds were determined in benzene solution by usual heterodyne-beat method.



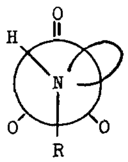
IV -NH-n-propyl
V -NH-n-pentyl
VI -NH-t-butyl
VII -N(ethyl)$_2$
VIII -O-n-propyl
IX -O-n-butyl
X -O-phenyl

A conceivable preferred conformation of the six-membered ring in these compounds should be either α or β.

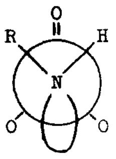


α β

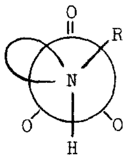
In addition to α and β conformers, rotational isomerism about the P-R bond should also be considered, such as following.



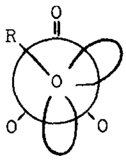
1



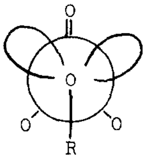
2



3



g



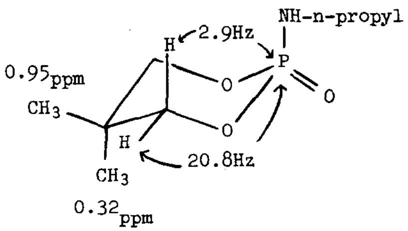
t

Calculated (9) and observed dipole moments of IV - X are listed in Table. In our calculations, all of the carbon atoms are assumed to be tetrahedral.

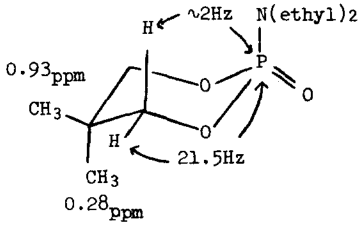
Class	Calcd. Moment (D)		Obsd. Moment (D)
A	α1 2.29	β1 3.89	IV 3.20
	α2 1.64	β2 3.50	V 3.11
	α3 3.41	β3 5.18	VI 3.08*
B	α 2.37 β 3.90		VII 3.88
C	αt 2.37	βt 5.40	VIII 5.46
	αg 2.41	βg 4.17	IX 5.48
			X 5.71

* The conformational study of this compound will be described elsewhere.

Although the values calculated for the rotational isomers about a P-N bond are incidentally the same in class B, the β conformation (possibly β2) of VII is evident. This conclusion may lead us to a convinction that the β conformer is the preferred one for class A compounds also (see Table), although α3 cannot be excluded by the dipole moment study alone. Quite similar pmr spectra between class A and B (VI gives a little different spectrum) may be considered as a strong support that these classes have similar conformations to each other. For example, some chemical shifts and coupling constants of IV and VII are given below.



IV



VII

100 MHz, C_6D_6 (TMS)

These parameters, expecially the values of the phosphorus-proton coupling constant, indicate that both IV and VII have one of the possible two chair-like forms (α and β) almost exclusively (1), and it should be quite strange if these compounds had the completely reversed configuration at the phosphorus atom to each other.

Class C has rather large dipole moments than expected. The best agreement between observed and calculated values are obtained when these molecules have βt conformation. However, βt structure seems to be quite anomalous as they may have unfavorable severe 1,3-diaxial repulsion interaction. In any case, β conformation is undoubtedly predominant also for class C.

The results, thus far obtained, show that the P=O bond farours the equatorial position than the axial one both in solution and in solid phase. We are now studying factors influencing the α ⟷ β equilibrium, which may afford further informations on the conformational preference of the P=O bond.

Acknowledgment

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