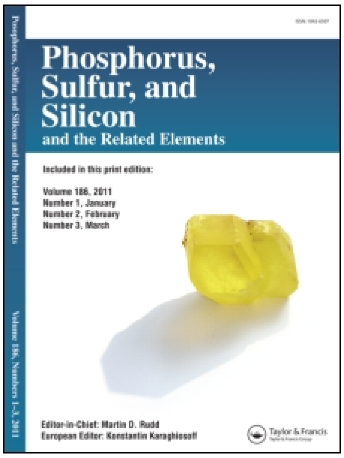

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Hydroxyphosphoranes tautomers of γ hydroxylated phosphoric esters - structure and acidity

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HYDROXYPHOSPHORANES TAUTOMERS OF γ HYDROXYLATED PHOSPHORIC ESTERS - STRUCTURE AND ACIDITY

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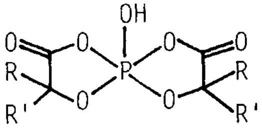
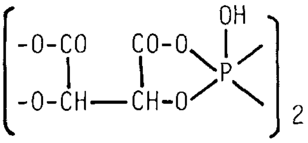
Abstract The crystal structure of the triethylammonium salts of hydroxyphosphoranes 1a and 2 was resolved by X Ray diffraction. The first one has a TBP geometry slightly deformed with the phosphorus atom at the center, and the second one is a polycyclic dimer containing two TBP which present the same deformations. In both cases, the $P-O^-$ bond lengths are short and dioxaphospholane rings planar. These two particular properties can be related to the strong Bronsted acidity of compounds 1a and 2. Effectively, the pKa of hydroxyphosphoranes 1a, 1b and 2, determined by potentiometrical titration in DMF or DMSO solutions are characteristic of strong acids.

INTRODUCTION

Hydroxyphosphoranes, tautomers of γ hydroxylated phosphoric esters are important intermediates in the hydrolysis of phosphoric esters of biological interest (nucleotides, enol phosphates, phosphates of lactic acid...) Many results and physico chemical properties of hydroxyphosphoranes of type 1 and 2 were described in our laboratory [1-2]. However, their crystal structure remained unresolved and the important question of their acidity was to be cleared.



1 : 1a : R = R' = Ph
1b : R = R' = CH_3



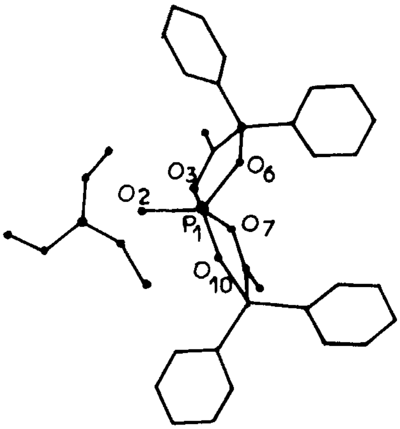
2

STRUCTURE

The crystalline structure of triethylammonium salts of phosphoranes 1a and 2 was determined by X Ray diffraction. The first one has a trigonal bipyramid (TBP) geometry slightly deformed with the phosphorus atom at the center (fig. 1), while the second is a polycyclic dimer compound containing two TBP (fig. 2). The deformations, regarding the idealized TBP, are not due, as it is the case for many spirophosphoranes, to a beginning Berry pseudo rotation [3]. They are more easely systematized by repulsion effects, of Gillespie type, between the anionic charge $P\text{-}O^-$ and the electrons of P-O bonds. For the two compounds, the bond lengths of the exocyclic $P\text{-}O^-$ are short (1.47 and 1.49 Å), and this illustrates the double bond character of the exocyclic P-O bond. The dioxaphospholane rings are nearly planar. This is unusual for dioxaphospholane rings involved in spirophosphoranic molecules and results from delocalization effect due to the conjugation of the carbonyl groups. Thus, the electron density around the phosphorus atom is lowered, and this must induce an high dissociation of the acid function P-O-H of the compounds 1a and 2.

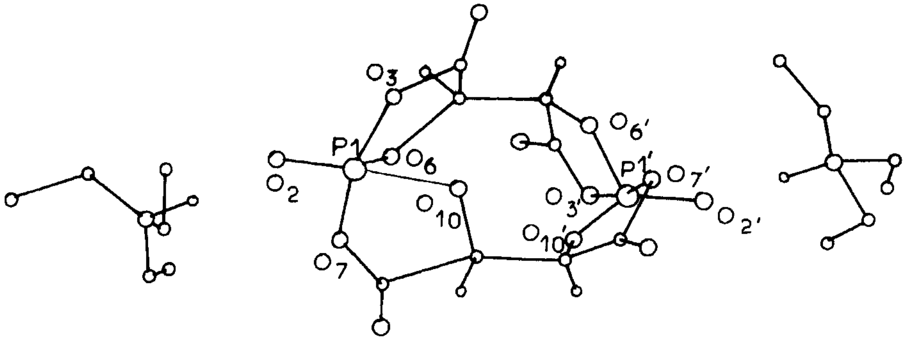
ACIDITY

We measured the pKa of the most stable compounds, 1a, 1b and 2. In order to explicit the influence of structure on acidities strength, we tried to prepare the compound 3, by oxydation of the parent hydridospirophosphorane. In fact, NMR proves that this derivative is present in the phosphoric ester form 3'. With triethylamine, however, it is quantitatively transformed in the hydroxyphosphorane salt 3", well characterized by ^{31}P NMR. Compounds 1a, 1b, 2 and 3,3', were titrated potentiometrically by triethylamine in DMF or (and) DMSO solution. The electrical scale was graduated in pH unities by titration of two standard acids : picric acid and dichloroacetic acid. The neutralization curves are characteristic of strong (1a, 2) medium (1b) or weak (3,3') acids. The



Bond angles (°)	
O(3)-P(1)-O(7)	169,9
O(10)-P(1)-O(6)	113,4

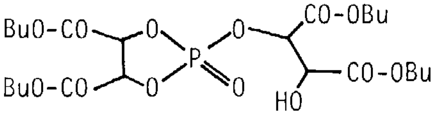
FIGURE 1 Crystalline structure of triethylammonium salt of <u>1a</u>



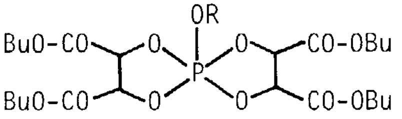
O(3)-P(1)-O(7)	170,9
O(3')-P(1')-O(7')	171,0
O(10)-P(1)-O(6)	116,4
O(10')-P(1')-O(6')	114,8

FIGURE 2 Crystalline structure of triethylammonium salt of <u>2</u>.

pKa values obtained by means of these curves are reported in table. The difference between pKa values of 1a, 2 and 3,3', demonstrate clearly the great influence of structure on acidity, little change in structure leading to a pKa variation of several units.



3'



3 : R = H, 3'' : R = $\mathrm{H}\overset{+}{\mathrm{N}}\mathrm{Et}_3$

TABLE pKa values of 1a, 1b, 2, 3,3', 4 and 5 in DMF and DMSO
4 : picric acid. 5 : dichloroacetic acid.

Compounds	1a	1b	2	3,3'	4	5
pKa DMF	2,5	3,9	2,2	7,4	$1,2^4$	$7,2^4$
pKa DMSO	-0,5	1,1	-0,6	4,4	$-0,3^4$	$5,9^4$

REFERENCES

1. A. Munoz, B. Garrigues and M. Koenig, Tetrahedron, 36, 2467 (1980).
2. A. Munoz, L. Lamandé, M. Koenig, R. Wolf and J. Brossas, Phosphorus and Sulfur, 11, 71 (1981).
3. R.R. Holmes, Acc. Chem. Res., 12, 257 (1979) and references there in.
4. B.G. Cox, Annu. Rep. Prog. Chem., 249 (1973) and references there in.

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