Stereoelectronic Effects in Phosphoric Acid and Phosphate Esters

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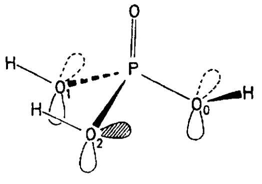
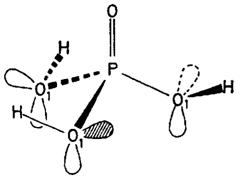
Summary Non-empirical computations show that the electronic properties of the P–O bonds in phosphoric acid and phosphate esters are markedly affected by conformation-dependent stereoelectronic effects which weaken the P–O bonds in monocyclic and especially in bridgehead bicyclic phosphates as compared to acyclic phosphates.

Phosphate esters undergo marked changes in properties (basicity, nucleophilicity, rates of hydrolysis, spectra) upon inclusion of the phosphate function into a monocyclic or a bridgehead bicyclic system. The steric and electronic consequences of the geometric constraints thus introduced have provided a basis for rationalizing the observed pattern of properties.[1,2] The role of π-bonding between the alkyl oxygen lone pairs and the phosphorus d-orbitals has been stressed.[2]

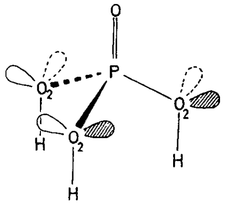
We report here that stereoelectronic effects similar to those which operate in the tetrahedral intermediates of hydrolytic reactions[3] are also present in phosphoric acid and in phosphate esters. Such effects should contribute to the observed differences in properties between acyclic, monocyclic, and bicyclic phosphates. They have been invoked recently for explaining the conformational properties of 1,3,2-dioxaphosphorinans.[4]



(1)



(2)



(3)

Figure. The labelling of the oxygen atoms refers to the number *n* of lone pairs which are *antiperplanar* to the C–O_n bond considered.

Ab initio computations† have been performed on the conformations (**1**), (**2**), and (**3**) of phosphoric acid and on conformation (**4**) [analogous to (**1**)] of trimethylphosphate. (**1**) and (**3**) may be considered respectively as models for monocyclic and bridgehead bicyclic phosphate esters. Computations with and without inclusion of *d* orbitals on phosphorus have been performed for species (**1**)—(**3**).

(i) In line with previous results[3,5] on C–X bond weakening and lengthening in a :Y–C–X fragment when the Y lone pair is antiperiplanar (*app*) to the polar C–X bond, one finds (Table) that the overlap population (O.P.)‡ of a P–O single bond decreases by about 0·04e for each oxygen lone pair *app* to this P–O bond. In a bridgehead bicyclic phosphate [see model (**3**)] the molecular structure imposes the condition that all 3 P–O bonds each have 2 *app* oxygen lone pairs (not taking into account the lone pairs on the P=O oxygen). These bonds are thus expected to be weaker and longer than in acyclic or monocyclic species which may take up other arrangements.

(ii) This stereoelectronic *app* lone pair effect on P–O bonds is present whether or not phosphorus *d*-orbitals are included in the basis set. It thus is not due to interaction of the alkoxy oxygen atoms with the *d*-orbitals on phosphorus. It is weaker, however, with *d*-inclusion than without.

(iii) The population analysis shows that the observed effect may be envisaged as the interaction of the *app* oxygen lone pair with the antibonding σ^* (P–O) orbital, similarly to previous results for other tetrahedral species.[3,5] The effect causes changes in the σ type but not in the π type O.P. of the P–O bond.

(iv) Comparison of species (**1**) and (**2**) with (**3**) shows that there is practically no stereoelectronic lone pair effect on the P=O bond when *d*-orbitals are included in the computation. Back-bonding in P=O may compensate the *app* lone pair weakening effect, but more strongly here than in P–O. The P=O oxygen appears to be less negatively charged in (**3**) than in (**1**) and (**2**) (Table) in agreement with experimental data and previous semi-empirical computations.[2,6]

(v) The role of *d*-orbitals, although not essential for the stereoelectronic effects discussed above, is important for bond strength. The O.P.'s of the P–O and P=O bonds increase very markedly, and the charges on P and O decrease, when *d*-orbitals are introduced. On the other hand the O.P. is much larger (twice or more) for P=O than for P–O. Thus the P=O bond indeed emerges as a 'double' bond in comparison to P–O; this is the case whether or not phosphorus *d*-orbitals are included in the computation, contrary to the usual picture which links 'double' bond character with $(d\text{–}p)\pi$ back-bonding. The O.P. of the P=O and P–O bonds contains *ca.* 60 and 45% π type overlap respectively, of which *ca.* 0·25 is of $(d\text{–}p)\pi$ type.

Table. Energies and population analysis for species (**1**)—(**3**)[a]

Species	(**1**)	(**2**)	(**3**)
Relative energy/ kcal mol^{-1}	6·1 (6·2)	0[b]	21·9 (24·2)
Overlap population			
Bond			
P–O	O(0) 0·577 (0·265) O(1) 0·531 (0·196) O(2) 0·448 (0·141)	0·544 (0·202)	0·484 (0·126)
P=O	1·068 (0·778)	1·066 (0·791)	1·072 (0·823)
Atomic charges			
P	1·76 (2·37)	1·76 (2·36)	1·74 (2·35)
O	−0·78 (−0·97)	−0·79 (−0·96)	−0·73 (−0·93)
O (OH)	O(0) −0·75 (−0·90) O(1) −0·75 (−0·90) O(2) −0·77 (−0·91)	−0·77 (−0·92)	−0·72 (−0·86)

[a] Values in parentheses are for (*sp*) and the others for (*spd*) calculations (see footnote).
[b] Total energy: −640·8819 a.u. (−640·6555 a.u.). The significance of the relative energies is limited to the forms computed here, since all geometries are idealized (see footnote).

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† Computations were performed with the program IBMOL, using a split *sp* basis set of contracted Gaussian functions (B. Roos and P. Siegbahn, *Theor. Chim. Acta*, 1970, **17**, 209) to which a set of *d* type functions (exponent: 0·57; *spd* set) was added on the P atom. Geometry: P=O 1·52; P–O: 1·58; O–H: 1·0 Å; since this study concerns orientational effects, all angles have to be taken as tetrahedral to ensure that the results are not complicated by angular constraint effects; all rotamers are in staggered form.

‡ A decrease or increase in overlap population of a bond may be taken as indicating that the bond is respectively weakened or strengthened (P. O. D. Offenhartz, 'Atomic and Molecular Orbital Theory,' McGraw Hill, New York, 1970).

(vi) Limited computations on trimethyl phosphate (**4**) show that the stereoelectronic effects found in phosphoric acid (**1**) are present almost unchanged in the phosphate esters. The same holds for the protonated derivatives of (**1**)–(**3**), $P(OH)_4^+$, which correspond to acid-catalysed hydrolysis of phosphate esters.

In conclusion, stereoelectronic effects resulting from rotameric orientation around P–O bonds are present in phosphate esters in addition to *d*-orbital and angular constraint effects. However, their influence on reactivities will depend on a complex interplay of these various effects and on the mechanism of the reactions: they may for instance contribute to the faster hydrolysis rate of $O{=}P(OCH_2)_3CMe$ as compared to a six-membered ring phosphate.[2] One may expect that similar orientational effects on molecular properties are present in phosphite esters $P(OR)_3$, and probably also in silicate $Si(OR)_4$, borate $B(OR)_4^-$, sulphate $SO_2(OR)_2$, and sulphite $SO(OR)_2$ esters, and other related tetrahedral or pyramidal species containing two or more geminal heteroatoms.

Especially interesting should be the cases of metal cation hydroxides and hydrates, which are presently being studied.

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[1] F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.

[2] J. G. Verkade, *Bioinorg. Chem.*, 1974, **3**, 165.

[3] J. M. Lehn, G. Wipff, and H. B. Bürgi, *Helv. Chim. Acta*, 1974, **57**, 493; J. M. Lehn and G. Wipff, *J. Amer. Chem. Soc.*, 1974, **96**, 4048.

[4] W. G. Bentrude, H. W. Tan, and K. C. Yee, *J. Amer. Chem. Soc.*, 1975, **97**, 573.

[5] S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffman, *J. Amer. Chem. Soc.*, 1973, **95**, 3806.

[6] R. L. Collin, *J. Amer. Chem. Soc.*, 1966, **88**, 3281; D. B. Boyd, *ibid.*, 1969, **91**, 1200.