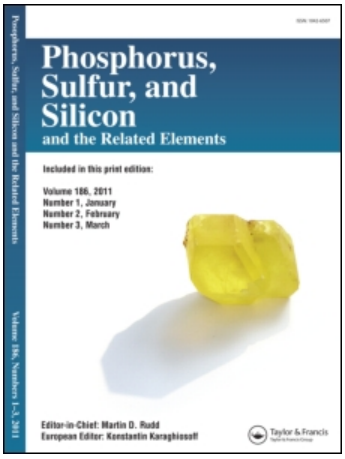

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Triarylphosphines : Molecular Geometry, Anodic Behavior and ESR Study of the Radical Cations

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TRIARYLPHOSPHINES : MOLECULAR GEOMETRY, ANODIC BEHAVIOR AND ESR STUDY OF THE RADICAL CATIONS

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Abstract A large series of triarylphosphines has been prepared and their geometry was studied by force field calculations. A very good agreement was found between the calculated and experimental (X Ray) geometries. The oxidation potentials were determined by electrochemical techniques and the corresponding cations were studied by ESR. Both the oxidation potentials and the ESR features were shown to depend strongly on the molecular geometry.

INTRODUCTION

Changing substituents on phosphorus ligands can cause significant changes in the behavior of the free ligands [1] and of their transition metal complexes [2]. Thus anodic oxidation of triphenylphosphine is irreversible and occurs at 1.40 V (in acetonitrile, v.s. S.C.E.) while the anodic oxidation of trimesitylphosphine is reversible and occurs at 0.78 V [1]. A dramatic change is also observed in the pKa of these phosphines going from 7.85 for the former to 13.10 for the later [3].

Using ESR the radical cation of triphenylphosphine is detectable only in matrice [4] while the radical cation of trimesitylphosphine can be detected in solution up to +60 ° C [1].

These changes result from the interplay of steric and electronic effects. For trimesitylphosphine according to X ray studies [5] the nonbonded repulsive interaction among the three bulky mesityl groups induces an important flattening of the phosphorus pyramid which is accompanied by an important increase in the contribution of the phosphorus 3p orbital to the HOMO.

In the course of our studies on the structure and reactivity of triarylphosphine cation radicals and owing to the great importance of triarylphosphines as ligands in many organometallic compounds we have examined the geometry of a large series of triarylphosphines (Table 1),their anodic behavior and the ESR characteristics of the corresponding cation radicals.

MOLECULAR GEOMETRY

Force field calculations have been successfully applied to model numerous classes of organic compounds but only a few limited studies have been devoted to organophosphines [6]. A MM2 parameter set for organophosphines has been recently proposed [6], but triphenylphosphine was the only triarylphosphine included in the series of organophosphines which were used to derive this parameter set.

Using this parameter set we calculated the geometry of four triarylphosphines **1** , **2** , **3**, **9** the stucture of which were already known from X ray studies. The experimental and calculated structures are listed in Table 2. A satisfactory agreement was found between the calculated and experimental values of $\Sigma\theta$, however except for **1** which was used to derive the parameter set, the calculated P--C bond lengths were too short, the discrepancy being particularly significant for **9**. We observed that this unexpected large

Table 1 : Ep (V vs SCE) and $\alpha°$ (MM2, see table 2) for some selected triarylphosphines PAr_3

Ar =

	1	2	3	4	5
Ep	1.40	1.26	1.34	1.19	1.19
α	*25.6*	*25.0*	*25.7*	*25.0*	*25.0*

	6	7	8	9	10
	1.20	0.88	1.07	0.78	0.99
	25.1	*19.3*	*25.20*	*19.3*	*24.9*

	11	12	13	14
	0.68		1.34	
	17.8	*23.5*	*28.4*	*26.6*

shortening of the P--C bond length was observed for all the triarylphosphines bearing two ortho methyl or two chlorine substituents on each aromatic ring.
To improve the fit between the experimental and calculated geometries within our series of triarylphosphines we modifed the MM2 phosphorus parameters. The best results were obtained including in the MM2 87 force field the parameters listed in Table 3.

The RMS for the mean value of the P-C bonds and the pyramidalization angle α were respectively $2 \cdot 10^{-2}$ Å and 0.39°. We found that the shortening of the P-C bond observed using the Allinger's parameters was related to the stretch-bend contribution which must be almost ignored to model phosphines.

ANODIC BEHAVIOUR

The oxidation potentials listed in Table1 were determined by pulse voltammetry which gave highly reliable recurring peak potential values. A significant decrease in the oxidation potential is observed as the number of methyl substituents on each aryl group increases. Thus the oxidation potential is reduced by 0.7 V, on going from triphenylphosphine **1**
reflects the change in energy of the HOMO, resulting from both the electronic and steric effects of the methyl substituents.
Owing to the complex interplay of the steric and electronic effects of the methyl substituents no straight-forward Hammett correlation was found with Ep when we considered the whole series of triarylphosphines. However a satisfactory correlation ($r = 0.97$) was obtained when Ep was plotted versus $\Sigma\sigma^+$, for the triarylphosphines **1**, **2**, **3**, **4**, **5**, **6**, **8** and **10** which all have almost the same pyramidalization angle α.
All the triarylphosphines bearing two ortho methyl groups on each aryl ligands exhibited reversible oxidation at moderate potential sweep rates (0.1 to 5 V s^{-1}).

Table 2: Calculated and Experimental Molecular Geometries of Triarylphosphines
1, **3**, **2**, **9**, **12**, **13**, **14**

	P-- C (Å)			Σ θ (deg)			α (deg)		
Phosphines	MM2 [i]	MM2 [j]	*RX*	MM2 [i]	MM2 [j]	*RX*	MM2 [i]	MM2 [j]	*RX*
1	1.828	**1.831**	*1.831*	303.8	**308.3**	*308.3*	26.58	**25.56**	*25.54*
2	1.829	**1.832**	*1.835*	303.4	**307.8**	*305.0*	26.9	**25.7**	*26.43*
3	1.828	**1.835**	*1.834*	308.7	**310.2**	*308.4*	25.42	**25.0**	*25.52*
9	1.808	**1.839**	*1.837*	337.6	**329.0**	*329.1*	16.18	**19.28**	*19.24*
12		**1.838**	*1.844*		**315.5**	*313.5*		**23.48**	*24.16*
13		**1.814**	*1.812*		**297.0**	*293.7*		**28.42**	*29.45*
14		**1.829**	*1.828*		**304.3**	*305.8*		**26.65**	*26.24*

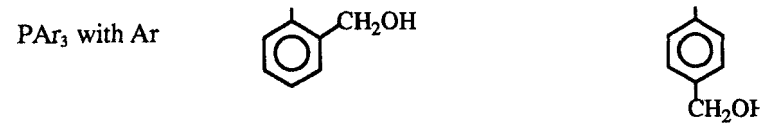
[i] Allinger's parameters , [j] parameters given in Table 3

Table 3. MM2 Force Field Parameters for Triarylphosphines

Bond-Stretching Parameters		
bond type	r_0 / Å	k_s / mdyn Å^{-1} molecule^{-1}
P----$C_{(sp^2)}$	1.82	4.0
Bond Bending Parameters		
bond angle	θ_0 / deg	k_θ / mdyn Å rad^{-2} molecule^{-1}
$C_{(sp^2)}$--P--$C_{(sp^2)}$	100	1.05
Torsional Constants		
torsion	V_1 / kJ mol^{-1}	V_2 / kJ mol^{-1}	V_3 / kJ mol^{-1}
$C_{(sp^2)}$-$C_{(sp^2)}$-$C_{(sp^2)}$-P	0	16.25	0
$C_{(sp^3)}$-$C_{(sp^2)}$-$C_{(sp^2)}$-P	0	16.25	0
Stretch-Bend Parameters		
type	$k_{s\text{-}b}$	
X-P-Y (5)	0.08	

We also studied triarylphosphines bearing phenyl rings substituted in the ortho or para positions with functionnal groups (scheme 1).

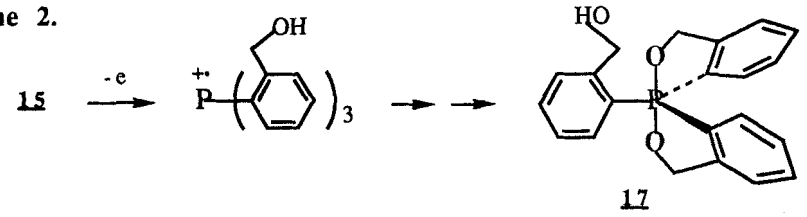
Scheme 1.



	15	**16**
Ep (V vs SCE)	0.88	1.38
α ° (MM2)	*24.76 (X Ray : 26.02)*	*25.69*

The dramatic difference in the oxydation potential in between **15** and **16** was attributed to a fast cyclisation of $\mathbf{15}^{+\bullet}$ giving rise to the 1-phenyl-8,8'-dimethyl-1,1'spirobis[1H,3H-2,1-benzoxaphosphole, **17**, wich was isolated in 50% yield after a preparative electrolysis of **15** (scheme 2).

Scheme 2.



ELECTRON SPIN RESONANCE STUDY

All the triarylphosphines exhibiting a significantly reversible anodic oxidation, yielded ESR signals when the oxidation was carried out within the cavity of an ESR spectrometer. Very intense ESR signals were observed for **7**, **9** and **11** in the temperature range -50 to + 60° C. The principal feature of these isotropic ESR spectra comprises a doublet resulting from a relatively large phosphorus coupling ($A_P \approx 240$ G) and these spectra can obviously be inferred to phosphoniumyl radicals.

Satisfactory frozen solution ESR spectra were obtained for the most persistent triarylphosphoniumyl radicals which allowed us to determine the anisotropic coupling B_P. From A_P and B_P we obtained the hybridization ratio for the phosphorus atom and the average pyramidilization angle[7] values for the radicals ($\alpha \approx 11°$). The electron loss is accompanied by a substantial flattening of the pyramidal geometry of the starting phosphine but the ensuing phosphoniumyl radical retains an equilibrium geometry which is still significantly bent.

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