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Molecular and electronic structures of radical-cations derived from diphosphines: a semi-empirical PM3 study

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Abstract

Semi-empirical PM3 calculations have been made of the molecular and electronic structures of $\text{Me}_2\text{P}(\text{CH}_2)_n\text{PMe}_2$ ($n = 0-3$) and of a similar related cyclic diphosphine, and of their radical-cations. When the configuration and conformation of the diphosphine are such that the nonbonded $\text{P} \cdots \text{P}$ distance is greater than ca 2.5 Å, the corresponding radical-cation has its SOMO strongly localised on a single phosphorus atom, with the two phosphorus atoms exhibiting markedly different geometries. When, however, the configuration and conformation are such that the non-bonded $\text{P} \cdots \text{P}$ distance is less than ca 2.5 Å, the radical cation has a symmetric structure with the SOMO delocalised over two equivalent phosphorus atoms; these symmetric conformers are stabilised over their asymmetric isomers by formation of a weak two-centre, three-electron $\sigma^*(\text{P}-\text{P})$ interaction. In the neutral diphosphine $\text{PhP}=\text{PPh}$ the HOMO is a phosphorus lone pair combination, rather than the $\pi(\text{P}-\text{P})$ bond: the corresponding radicalcation has its SOMO delocalised in the CPPC plane.

Introduction

Exposure of tertiary phosphines, R_3P , to γ irradiation in glasses or in frozen solution can give rise to a wide range of chemical processes, amongst which are the formation of radical-cations R_3P^+ and of dimer-cations $[\text{R}_3\text{P}-\text{PR}_3]^+$ [1–3]. MNDO calculations on representative examples of such cations have shown [4] that the dimer-cations $(\text{R}_3\text{P})_2^{+ \cdot}$, and analogous cations $[(\text{RO})_3\text{P}]_2^{+ \cdot}$ derived from trialkylphosphites $(\text{RO})_3\text{P}$, are all σ^* radicals having highly symmetrical skeletal structures with the SOMO strongly confined to the $\text{P}-\text{P}$ bond.

It is therefore of interest that exposure of the diphosphines $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ to similar γ -irradiation has recently been reported [5]. For the radical-cation $[\text{Ph}_2\text{PCH}_2\text{PPh}_2]^{+ \cdot}$ the ESR spectrum was interpreted in terms of a SOMO localised on only one phosphorus atom, while for $[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]^{+ \cdot}$ two forms were reported. In one, the SOMO was localised on one phosphorus atom, analogous to the radical-cations derived from monophosphines, while in the other the SOMO was delocalised over both phosphorus atoms in a manner reminiscent of the dimer-cations $(\text{R}_6\text{P}_2)^{+ \cdot}$. Features of particular interest here are the structures of the localised radical-cations, and the factors influencing the choice between localised

and delocalised forms: in the present paper we report semi-empirical SCF calculations, made using the PM3 method [6], intended to resolve these questions. We also report, briefly, similar calculations on the radical-cations $(\text{ArPPAr})^{+\cdot}$ derived from diaryldiphosphenes [7]. The properties of species $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]^{+\cdot}$ were modelled using $[\text{Me}_2\text{P}(\text{CH}_2)_n\text{PMe}_2]^{+\cdot}$ and those of $(\text{ArPPAr})^{+\cdot}$ [$\text{Ar} = 2,4,6\text{-(Me}_3\text{C)}_3\text{C}_6\text{H}_2$] were modelled using $(\text{PhPPP})^{+\cdot}$.

Calculations

All calculations were made using the PM3 method [6,8] as implemented in Version 5.0 of the MOPAC system [9]. UHF wavefunctions were employed for all open-shell species and, except where specified otherwise, all geometric variables were simultaneously optimised without the imposition of any constraints. The PRECISE option was employed throughout. The diphosphine radical cations all had calculated $\langle s^2 \rangle$ values in the range 0.752–0.755 with the exceptions of **9**, 0.762 and $\text{Me}_4\text{P}^{+\cdot}$, 0.766, indicative of very little spin contamination of the doublet wave-functions.

Results and discussion

$\text{Me}_2\text{P}(\text{CH}_2)_n\text{PMe}_2$ ($n = 1-3$) and their radical-cations

The neutral diphosphine $\text{Me}_2\text{PCH}_2\text{PMe}_2$, when freely optimised, converged to a structure of C_{2v} symmetry, with a PCP angle of 111.1° , and a $\text{P} \cdots \text{P}$ distance of 3.119 Å (leading values of calculated parameters are summarised in Table 1). The in-phase combination of phosphorus lone pair orbital is the HOMO, at -8.67 eV, and the out-of-phase combination is the next occupied orbital at -8.82 eV. This ordering is probably a consequence of a destabilising interaction between the in-phase lone pair orbital combination with the out-of-phase combination of $\sigma(\text{C-H})$ orbitals of the central CH_2 group, rather similar to that discussed by Hoffmann for the case of singlet trimethylene [10]. When, however, the structure of the corresponding radical-cation was optimised, the C_{2v} symmetry was reduced to C_s , as the resulting radical clearly had a localised SOMO.

The structure calculated for $[\text{Me}_2\text{PCH}_2\text{PMe}_2]^{+\cdot}$ (Fig. 1) shows that one phosphorus atom, P_a , is still high pyramidal with a sum of bond angles of 303.3° (cf 301.3° in the neutral compound) while the other, P_b , approaches planarity with a bond angle sum of 342.1° (cf 360.0° calculated for $\text{Me}_2\text{P}=\text{CH}_2$, and 341.7° for $\text{Me}_2\text{P}^{+\cdot}$).

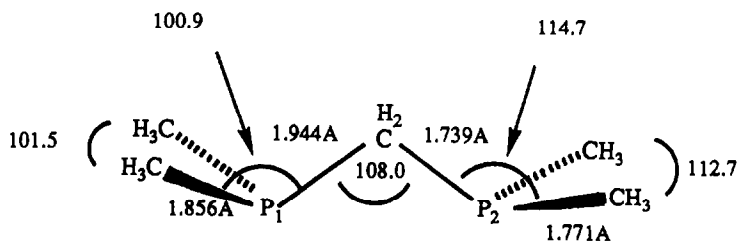


Fig. 1. The structure of $(\text{Me}_2\text{PCH}_2\text{PMe}_2)^{+\cdot}$.

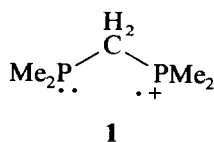
Table 1

Calculated properties for simple diphosphines and their radical cations

	Skeletal symmetry	$d(\text{P}-\text{C})$ (Å)	$d(\text{C}-\text{C})$ (Å)	$\angle(\text{PCX})$ (°)	$d(\text{P}\cdots\text{P})$ (Å)	$p(\text{P}\cdots\text{P})^a$	$\rho[\text{P}(3s)]^b$	ΔH_f^c (kJ mol ⁻¹)
$\text{Me}_2\text{PCH}_2\text{PMe}_2$	C_{2v}	1.891	-	111.1	3.119	0.008	-	-172.1
$(\text{Me}_2\text{PCH}_2\text{PMe}_2)^{+\bullet}$	C_s^c	$\left\{ \begin{array}{l} 1.944 \\ 1.739 \end{array} \right.$	-	108.0	2.982	0.024	$\left\{ \begin{array}{l} +0.0024 \\ +0.1563 \end{array} \right.$	+570.6
<i>cisoid</i> - $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$	C_2	1.904	1.492	103.4	2.517	0.081	-	-163.4
<i>cisoid</i> - $[\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2]^{+\bullet}$	C_{2v}	1.874	1.501	101.2	2.618	0.288	+0.1343($\times 2$)	+457.2
<i>transoid</i> - $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$	C_i	1.902	1.489	109.5	4.524	0.015	-	-190.8
<i>transoid</i> - $[\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2]^{+\bullet}$	C_i^c	$\left\{ \begin{array}{l} 1.921 \\ 1.803 \end{array} \right.$	1.491	106.2 114.1	4.432	0.011	$\left\{ \begin{array}{l} -0.004 \\ +0.1335 \end{array} \right.$	+572.1
<i>cisoid</i> - $\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2$	C_i	1.915	1.508	123.6	2.502	0.082	-	-164.0
<i>cisoid</i> - $[\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2]^{+\bullet}$	C_{2v}	1.875	1.519	115.0	2.203	0.316	+0.1513($\times 2$)	+448.1
<i>transoid</i> - $\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2$	C_2	1.898	1.508	108.0	5.541	0.001	-	-210.0
<i>transoid</i> - $[\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2]^{+\bullet}$	C_s^c	$\left\{ \begin{array}{l} 1.908 \\ 1.786 \end{array} \right.$	1.504 1.520	106.4 108.0	5.387	0.001	$\left\{ \begin{array}{l} +0.0001 \\ +0.1427 \end{array} \right.$	+557.3
$\begin{array}{c} a \\ \text{MeP} \\ b \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{PMe}$	C_s	$\left\{ \begin{array}{l} 1.908(a) \\ 1.876(b) \end{array} \right.$	1.495	115.2(PCC) 112.6(PCP)	3.122	0.031	-	-123.6
$\left[\begin{array}{c} a \\ \text{MeP} \\ b \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{PMe} \right]^{+\bullet}$	C_s	$\left\{ \begin{array}{l} 1.871(a) \\ 1.846(b) \end{array} \right.$	1.501	101.2(PCC) 74.3(PCP)	2.230	0.261	+0.1063($\times 2$)	+639.4
Me_2P_2	C_2^d	-	-	-	2.156	0.963	-	-146.1
$(\text{Me}_2\text{P}_2)^{+\bullet}$	C_{2h}^e	-	-	-	2.122	0.746	+0.0283($\times 2$)	+574.7
PhPPPh	C_{2h}	1.829	-	108.8	1.926	1.915	-	+369.3
$(\text{PhPPPh})^{+\bullet}$	C_{2h}	1.739	-	120.8	1.878	1.667	+0.0292($\times 2$)	+1088.6

^a P...P bond order. ^b Spin density at phosphorus 3s orbital. ^c Two sets of results for $d(\text{P}-\text{C})$ and $\rho[\text{P}(3s)]$ refer to two distinct P atoms. ^d Dihedral angles of Me from C_2 axis: $\pm 100.9^\circ$, $\pm 150.6^\circ$ (see text). ^e Dihedral angles of Me from C_2 axis: $\pm 31.4^\circ$, $\pm 148.6^\circ$.

The flattened phosphorus atom not only carries a much higher net positive charge than the pyramidal phosphorus, +1.33 versus +0.55, but is also the site of the highly localised SOMO, which makes an angle of 103.3° with the corresponding P-CH₂ bridge bond. The flattened P atom carries a very high P(3s) spin density (Table 1) whereas that on the other phosphorus atom is negligibly small: all the evidence therefore points to a highly localised radical-cation (1):



Two stable conformations were found for the neutral bisphosphinoethane Me₂PCH₂CH₂PMe₂. Of these the more stable, by ca. 27 kJ mol⁻¹, was the centrosymmetric staggered *anti* conformation having a dihedral angle $\delta(\text{PCCP})$ of 180° and a P...P distance of 4.524 Å; the other minimum was close to an eclipsed conformation with $\delta(\text{PCCP})$ of 26.1° and a much shorter P...P distance, 2.517 Å. The stability order of these conformers is, however, reversed upon formation of the corresponding radical-cations.

The eclipsed form was found to be the more stable conformation of the radical-cation by some 115 kJ mol⁻¹: this conformer has *C*_{2v} symmetry (i.e. $\delta(\text{PCCP})$ is zero), with a P...P distance of 2.618 Å, associated with a bond order of 0.288, and a SOMO symmetrically delocalised over two phosphorus atoms. The in-phase combination of the phosphorus lone pair orbitals of *a*₁ symmetry is doubly occupied, while the out-of-phase combination, of *b*₂ symmetry is singly occupied: the double occupation of the bonding P...P orbital accounts both for the high P...P bond order, and for the enhanced stability of this conformer over the *anti* form. Whereas in the eclipsed, neutral Me₂P(CH₂)₂PMe₂, the CPC bond angles are typical of those in non sterically demanding tertiary phosphines with a calculated angle-sum of 300.6° , in the radical-cation the geometry at phosphorus is much more nearly pseudo-tetrahedral (Fig. 2): the lobes of the SOMO subtend an angle of 123.2° , indicative of a substantially bent P-P bond [5].

In the extended-chain radical-cation, the two phosphorus atoms have structural characteristics very similar to those in 1, above. The phosphorus atom at which is localised the SOMO, has a calculated sum of CPC bond angles of 342.0° , a net charge of +1.22, and a high P(3s) spin density: the other phosphorus atom, which carries a normal localised lone pair has a calculated sum of valence angles of 302.4° , a net charge of +0.49, and carries negligible spin density.

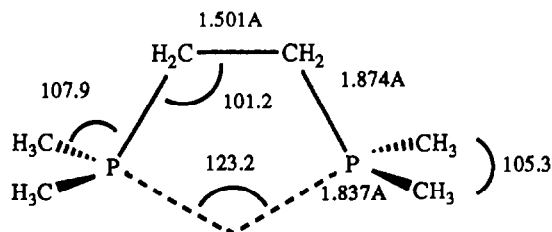
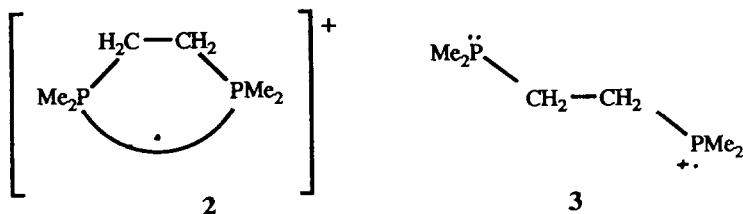
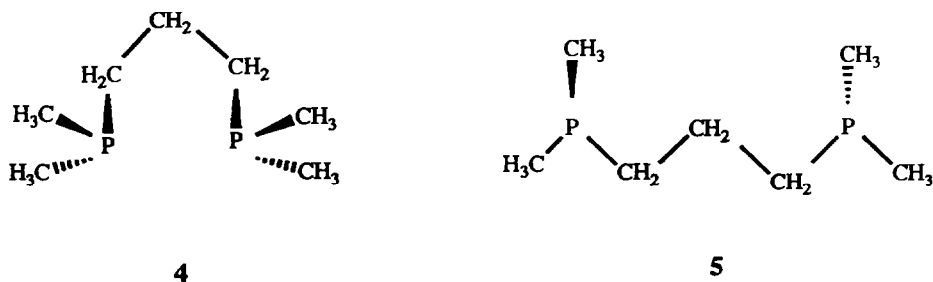


Fig. 2. The structure of 2 showing the angle subtended by the principal lobes of the SOMO.

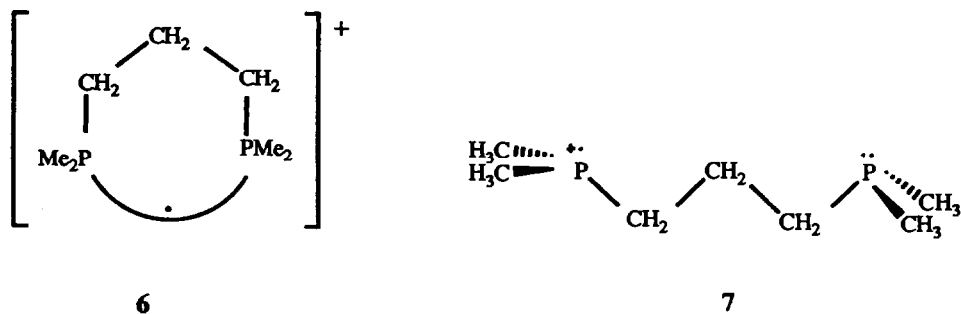
Thus, whereas the *cis* form of this radical-cations a bent two-centre, three-electron σ^* P–P bond (2) analogous to that in $[\text{Me}_3\text{P-PMe}_3]^+$ [3,4], the *anti* form contains a highly localised positive hole (3), just as for 1.



Extensive exploration of the potential energy surface of the bis-phosphine propane $\text{Me}_2\text{P}(\text{CH}_2)_3\text{PMe}_2$ revealed only two minima, the all *cisoid* form 4, having C_s skeletal symmetry, and the chain-extended form 5, of C_2 skeletal symmetry. Conformer 5 with a $\text{P} \cdots \text{P}$ distance of 5.541 Å, is more stable by 46 kJ mol⁻¹ than conformer 4 whose $\text{P} \cdots \text{P}$ distance is only 2.502 Å.



As for the bisphosphinoethane discussed earlier, the stability order of the conformers is reversed upon radical-cation formation. Ionisation of 4 leads to a delocalised radical-cation of exact C_{2v} symmetry, in which the $\text{P} \cdots \text{P}$ distance is 2.203 Å, with a $\text{P} \cdots \text{P}$ bond order of 0.316. The SOMO is delocalised over the two phosphorus atoms, and the SOMO lobes meet at an angle of 145.1°, to give a slightly bent two-centre, three-electron σ^* P–P bond (6). Ionisation of 5 provides a radical-cation with a strongly trapped positive hole (7).



The foregoing results all suggest that the formation of localised as opposed to delocalised radical-cations, as observed for $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and $\text{Ph}_2(\text{CH}_2)_2\text{PPh}_2$, respectively [5], depends less upon the number of bridging atoms between the phosphorus centres than upon the through-space distance between the phosphorus atoms; this in turn is strongly dependent upon conformation in $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ for $n > 2$.

This idea was tested in two ways. First, the cyclic diphosphine **8**, having both monomethylene (cf $\text{Me}_2\text{PCH}_2\text{PMe}_2$) and dimethylene bridges (cf $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$) between the phosphorus atoms, was studied. The neutral diphosphine optimised to a structure of overall C_s symmetry having a $\text{P}\cdots\text{P}$ distance of 3.122 Å.



When the corresponding radical-cation was optimised, the C_s molecular symmetry was retained but with the carbon atom of the unique methylene group now displaced from the PCCP plane by 0.205 Å, whereas in neutral **8** this carbon atom is coplanar with the rest of the ring. Associated with this ring puckering into the envelope conformation typical of saturated five-membered rings is a reduction in the $\text{P}\cdots\text{P}$ distance to 2.23 Å. At this distance the SOMO is symmetrically delocalised over the two phosphorus atoms: the net $\text{P}\cdots\text{P}$ bonding so produced is reflected in the $\text{P}\cdots\text{P}$ bond order of 0.261. Again a weak and bent two-centre, three-electron σ^* bond is formed upon ionisation to give the radical cation **9**.

Secondly the electronic properties of $(\text{Me}_2\text{PCH}_2\text{PMe}_2)^{+\bullet}$ were studied as a function of the PCP bond angle. While the calculated energy of neutral $\text{Me}_2\text{PCH}_2\text{PMe}_2$ increased monotonically, as expected, as the PCP angle was reduced from the equilibrium value, for the radical-cation the energy initially rose and the positive hole remained trapped in an asymmetric structure; however, for $\text{P}\cdots\text{P}$ distances of ca 2.4 Å (corresponding to a PCP angle of ca 85°) the energy suddenly dropped by ca 40 kJ mol^{-1} as the symmetric, delocalised radical-cation was formed. Even when the geometric structure was constrained to C_{2v} symmetry, the electronic structure was markedly asymmetric for $\text{P}\cdots\text{P}$ distances greater than ca 2.4 Å. Normally, formation of the symmetric radical will be prevented by the large energy barrier which must be overcome before the phosphorus atoms are sufficiently close.

For non-cyclic species $[\text{Me}_2\text{P}(\text{CH}_2)_n\text{PMe}_2]^x$ ($x = 0, 1$) at equilibrium, the energy differences between the radical-cation and the neutral parent fall into two distinct groups. For localised radical-cations in which the SOMO is largely confined to a single phosphorus atom, the values of Δ (ΔH_f) lie in the range +742.7 kJ mol^{-1} (for $n = 1$) to +767.3 kJ mol^{-1} (for $n = 3$), while for the delocalised radical-cations having $n = 2$ and 3 the Δ (ΔH_f) values are +620.6 and +612.0 kJ mol^{-1} , respectively. This is another reflection of the very much enhanced stability conferred upon these radical-cations by weak $\text{P}\cdots\text{P}$ bond formation.

Me₄P₂ and its radical-cation

Three conformations were found for the neutral tetramethyldiphosphine Me₄P₂, of respectively C₂, C_{2v} and C_{2h} molecular symmetry, of which the C₂ conformer was lower in energy than the C_{2v} form by only 1.3 kJ mol⁻¹, and lower than the C_{2h} form by 10.5 kJ mol⁻¹, suggesting that a wide range of conformations will be significantly populated at ambient temperature. This conclusion is consistent with the results of a gas-phase electron diffraction study, which was unable to establish the conformation with certainty because of the large amplitude motions about the P–P bond [11].

Ionisation of any of these conformers led, upon free optimisation to the same radical-cation of C_{2h} symmetry, in which the SOMO of a_g symmetry comprises equal populations from the two phosphorus atoms. In the neutral C_{2h} conformer the phosphorus lone pairs provide two orbital combinations of respectively a_g and b_u symmetry, of which the a_g combination is the HOMO: ionisation to (Me₄P₂)⁺ preserves the b_u combination as a doubly occupied orbital, with the a_g combination dominating the composition of the SOMO. The P–P bond order is less, at 0.746, than that 0.963 in the neutral diphosphine, but there is no straightforward pictorial representation of the electronic structure of (Me₄P₂)⁺: because of the comparatively low molecular symmetry, there is mixing between the P–P bond orbitals, the lone pair orbitals and the C–P bond orbitals in symmetry classes a_g and b_u. This accounts for the interaction between “lone pair” ionisation and the reduction in the P–P bond order.

PhP=PPh and its radical-cation

Free optimisation of neutral Ph₂P₂ gave a *trans* geometry of overall C_{2h} molecular symmetry, with P=P and P–C distances of 1.926 Å and 1.829 Å, respectively. These are close to the experimentally determined values in Ar₂P₂ (Ar = 2,4,6-(Me₃C)₃C₆H₄) [12] and in [(Me₃Si)₃C]₂ P₂ [13]. The calculated PPC angle is 108.8°, and the HOMO is the in-phase combination of phosphorus lone-pair orbitals, of a_g symmetry: as in Me₄P₂ and its radical-cation, the low molecular symmetry leads to mixing of the σ(P–P), P–C, and phosphorus lone pair orbitals.

When the radical-cation (Ph₂P₂)⁺ was optimised (with the phenyl rings held as hexagons) the resulting structure retained C_{2h} symmetry, but with a PPC bond angle increased to 120.8° and the P–P bond order reduced from 1.915 to 1.667 [cf. (Me₄P₂)⁺]. The SOMO is delocalised over the two equivalent phosphorus atoms, and is dominated by the in-phase combination of lone-pair orbitals. The P–P π-orbital is doubly occupied in (Ph₂P₂)⁺: this is consistent with the deductions made [7] from the ESR spectra of (Ar₂P₂)⁺. However, it was further suggested [7] that, on the assumption of complete orbital following, the PPC angle in this radical-cation is increased to ca 150°, although the calculations here on (R₂P₂)⁺ indicate an angle of 120.8° in (Ph₂P₂)⁺ and 122.6° in (Me₂P₂)⁺. The difference is attributable partly to the fact that the SOMO in (Ph₂P₂)⁺ is not localised exclusively [7] on the phosphorus atoms but also interacts with the π-systems, of the aryl substituents, and partly to the assumptions used [7] in the calculation of the bond angle from the ESR data.

References

- 1 A. Begum, A.R. Lyons and M.C.R. Symons, *J. Chem. Soc. (A)*, (1971) 2290.
- 2 A.R. Lyons and M.C.R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 68 (1972) 1589.

- 3 A. Hasegawa, G.D.G. McConnachie and M.C.R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 80 (1984) 1005
- 4 C. Glidewell, *J. Chem. Soc., Perkin Trans. 2*, (1985) 551.
- 5 C.J. Rhodes and M.C.R. Symons, *J. Chem. Soc., Chem. Commun.*, (1989) 1393.
- 6 J.J.P. Stewart, *J. Comp. Chem.*, 10 (1989) 209.
- 7 C.J. Rhodes, *J. Chem. Soc., Chem. Commun.*, (1989) 949.
- 8 J.J.P. Stewart, *J. Comp. Chem.*, 10 (1989) 221.
- 9 J.J.P. Stewart, QCPE No. 455, Version 5.0.
- 10 R. Hoffmann, *J. Am. Chem. Soc.*, 90 (1968) 1475.
- 11 A. McAdam, B. Beagley and T.G. Hewitt, *Trans. Faraday Soc.*, 66 (1970) 2732.
- 12 M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, 103 (1981) 4587.
- 13 A.H. Cowley, J.E. Kilduff, J.G. Lasch, S.K. Mehrotra, N.C. Norman, M. Pakulski, B.R. Whittlesey, J.L. Atwood and W.E. Hunter, *Inorg. Chem.*, 23 (1984) 2582.