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Preparation and Structure of Certain Phosphorus-centred Radical Cations

An Electron Spin Resonance Study

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Exposure of dilute solutions of various trivalent phosphorus derivatives, PL_3, in fluorotrichloromethane to ^{60}Co γ-rays at 77 K gave the corresponding cations, $[\cdot PL_3]^+$, characterised by their e.s.r. spectra. The spectra establish that the SOMO for these cations is considerably localised on phosphorus, which contributes extensive atomic 3*s* and 3*p* character. The results confirm and extend previous studies using sulphuric acid matrices. The tendency for these cations to react with corresponding neutral molecules to give σ^* dimer-cations $[L_3P\overset{\cdot}{-}PL_3]^+$ is also confirmed.

The structures of these species are discussed and compared with those of related radicals.

Some time ago we showed that certain radicals thought to be radical cations can be prepared by exposing dilute solutions in sulphuric acid to ^{60}Co γ-rays at 77 K.[1-3] In particular, species with e.s.r. parameters of the type expected for $R_3P^{\cdot +}$ cations were obtained from solutions of PH_3, PEt_3 and PPh_3. The mechanisms of these reactions remain unclear. One possibility is direct electron transfer between the substrate and $HSO_4\cdot$ radicals

$$PR_3 + HSO_4\cdot \rightarrow \cdot PR_3^+ + HSO_4^-. \qquad (1)$$

Another is hydrogen-atom abstraction from the protonated phosphine

$$HPR_3^+ + HSO_4\cdot \rightarrow \cdot PR_3^+ + H_2SO_4. \qquad (2)$$

However, many other endeavours to prepare radical cations by this procedure failed, an example being our attempts to prepare alcohol radical cations[4] $(R\dot{O}H)^+$ and ether radical cations $(R_2\dot{O})^+$.[5] A more satisfactory general procedure for preparing matrix-isolated radical cations involves exposing dilute solutions of the parent molecules in solvents such as freon ($CFCl_3$) or SF_6 to ionizing radiation at 77 K or lower temperatures. Although solvents of this type were used some time ago for optical studies,[6,7] it is only in the past few years that their great utility for e.s.r. studies has been appreciated.[8-12]

We have already reported the successful preparation of $\cdot PMe_3^+$ by this method.[13] Here we extend this work to several other phosphines. The results are generally similar to those obtained from centres in sulphuric acid and we conclude that this solvent is satisfactory for the phosphines except that resolution is poor. We failed to prepare $\cdot PH_3^+$ in freon, but conclude that the results assigned to this species in sulphuric acid are almost certainly correct.

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EXPERIMENTAL

Phosphines were of the highest purity available and were not, in general, further purified. Purity was checked by n.m.r. or infrared spectroscopy. Dilute solutions (generally *ca.* 0.1 % mole fraction except when the effect of increasing concentration was under study) of the phosphines in $CFCl_3$ were degassed and cooled as small beads to 77 K, at which temperature they were exposed to γ-rays in a Vickrad ^{60}Co source with doses up to *ca.* 1 Mrad.

E.s.r. spectra were measured at 77 K on a Varian E-109 spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe, which were standardized with a sample of DPPH. Samples were annealed by decanting the coolant and recooling to 77 K whenever significant changes in the e.s.r. features were detected. This process was continued until the samples melted, all features then being lost irreversibly (*ca.* 160 K).

RESULTS AND DISCUSSION

It is so well established that this technique furnishes either the parent radical cations or some unimolecular reaction product thereof, that this is assumed in the following discussion. We expect the parent cations, $\cdot PR_3^+$, to have pyramidal structures and hence that the SOMO (semi-occupied molecular orbital) will have a major contribution from the 3*s* orbital on phosphorus. This will confer a large ^{13}P hyperfine coupling and we focus attention on such species. In most cases, signals in the free-spin region were also obtained, but these were generally thought to be due to radical cations formed from freon impurities and are not considered in the following.

EFFECT OF CONCENTRATION

In all cases when the concentration of phosphine was increased new features outside the doublet features assigned to the parent cations grew in [*cf.* fig. 1(*a*)]. These are assigned to the $M_I = \pm 1$ features of the dimer cations formed by reaction with the parent phosphine

$$\cdot PR_3^+ + PR_3 \rightarrow (R_3P\cdot PR_3)^+. \qquad (3)$$

We have previously shown that the $\cdot PR_3^+$ cations cannot be detected when the pure phosphines, PR_3, are irradiated, the sole electron-loss centres being identical with those identified as the dimer cations.[14] These radicals are thought to have a weak phosphorus–phosphorus σ bond, the SOMO being the σ^* orbital. We therefore describe them as σ^* radicals.[15] Their propensity to form is shared with sulphur[16, 17] and halogen[18] derivatives, but not, in general, with nitrogen and oxygen derivatives.[5, 18]

EFFECT OF SOLVENT

The ionization potentials of these phosphines are well below those for $CFCl_3$ and CCl_4, and hence both these solvents were used. To our surprise, there were several differences especially for $\cdot P(OMe)_3^+$ radicals. We have previously observed a weak, extra doublet splitting tentatively assigned to hyperfine coupling to an extra ^{19}F nucleus of a solvent molecule for $C_2F_4^+$ cations,[19] and in other cases a quartet splitting has been assigned to $^{35/37}Cl$ hyperfine coupling.[20] However, in the present case the differences do not seem to be associated with strong matrix interactions of this sort.

TRIALKYLPHOSPHINES

The e.s.r. spectrum assigned to the trimethylphosphine cation in $CFCl_3$ is shown in fig. 1(*a*). This is very similar to that obtained from sulphuric acid solutions, except that the ^1H hyperfine coupling is clearly resolved, whereas only broad lines were

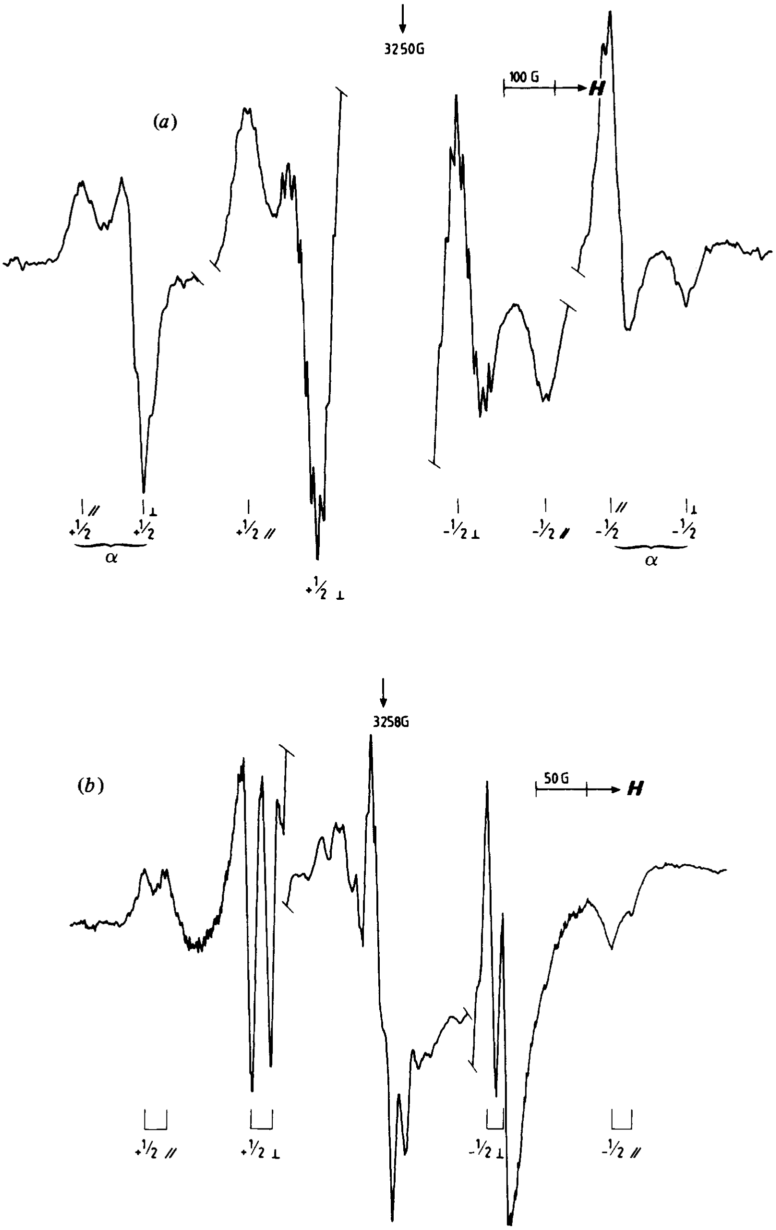


Fig. 1. First-derivative X-band e.s.r. spectra for dilute solutions of (*a*) PMe_3 and (*b*) PPh_3 in freon ($CFCl_3$) after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $\cdot PMe_3^+$ and $\cdot PPh_3^+$, respectively. Features for the dimer cation $(Me_3P\dot{-}PMe_3)^+$ (α) can also be seen in (*a*), and the extra doublet splitting tentatively assigned to ^{19}F coupling can be seen in (*b*).

obtained from the acid glasses. The outer features in the spectrum in fig. 1(*a*) are assigned to the dimer cations, $(Me_3P\dot{-}PMe_3)^+$: these features were selectively lost on dilution. Relatively intense central features are due partly to the '$M_I = 0$' ($|1,0\rangle$ and $|0,0\rangle$) features for the dimer and partly to impurity centres. On annealing dilute solutions, dimer-cation features grew in at the expense of the monomer-cation features, but no other significant changes were detected.

Results for triethylphosphine were similar, except that the lines were broader and proton hyperfine coupling was not resolved.

The results for the tri-n-butyl derivative are of some interest since there is a clear fall in $A_\parallel$ and $A_\perp$(^{31}P). This is due, largely, to a fall in A_{iso}, suggesting a slight flattening of the radical. We suggest that this is caused by steric interactions between the bulky ligands. The coupling to two protons (27 G), even if the most favourable overlap is assumed ($\theta = 0$), is larger than that predicted from the average coupling of 11.5 G for $\cdot PMe_3^+$ (*i.e.* 23 G). This accords with our postulate of a flattening at phosphorus and the concept that hyperconjugation becomes more effective on flattening.

TRIPHENYLPHOSPHINE

Again, well defined ^{31}P parallel and perpendicular features were obtained. Initially these were not further resolved, but after annealing to *ca.* 120 K a well defined doublet splitting of *ca.* 30 G was resolved [fig. 1(*b*)] for solutions in $CFCl_3$. The ^{31}P e.s.r. parameters are similar to those we obtained from solutions of PPh_3 in sulphuric acid[3] and to those assigned to $\cdot PPh_3^+$ cations in irradiated crystals of $Ph_3P{-}BF_3$ by Lucken and coworkers[21] (see table 1). The extra doublet splitting is unexpected. It was not observed for the radical in tetrachloromethane, so we are inclined to assign it to ^{19}F coupling from a single $CFCl_3$ molecule. An alternative is that this stems from coupling to ring protons, which is less in CCl_4. We could envisage a situation in which only one Ph group participates in delocalisation, in which case coupling to the *para* proton should dominate. However, a splitting of *ca.* 30 G is far too large for such a structure.

As with the results for $C_2F_4^+$,[19] we are at a loss to understand why these particular radicals should exhibit such a specific interaction when very similar species do not. Furthermore, any such interaction should, in our view, be of a charge-transfer type, in which case coupling to a $^{35/37}$Cl nucleus would be expected rather than to ^{19}F.

As with the other cations, dimer features were obtained on annealing, or with more concentrated solutions. These exhibited no extra splittings.

TRIMETHYL- AND TRIETHYL-PHOSPHITE

Results for the $\cdot P(OMe)_3^+$ cation are most interesting. In CCl_4, very sharp parallel and perpendicular features were obtained [fig. 2(*a*) (species A)]. However, for $CFCl_3$ solutions only weak lines were detected in those regions [fig. 2(*b*)], there being a series of features, all reasonably assigned to $\cdot P(OMe)_3^+$ cations, with reduced ^{31}P coupling (table 1), the dominating set being described as species B.

In an attempt to understand these features, we studied a range of mixed $CCl_4 + CFCl_3$ solvent systems. As $CFCl_3$ was added to CCl_4, so the sharp lines for species A broadened without shifting and features for species B, the major freon species, grew in. The way this trend occurred is indicated in fig. 3. The extra, minor features were only observed in almost pure freon solutions and we ignore them in the present discussion. Species A is still present in low abundance in pure freon solutions.

We suggest that there are two major conformations adopted by $\cdot P(OMe)_3^+$, one being favoured in CCl_4 and the other in $CFCl_3$. Since the former solvent has effectively spherical molecules we tentatively propose the more spherical structure (I) for solutions in CCl_4 and the more oblate structure (II) for freon solutions. It is curious

Table 1. E.s.r. parameters of some radical cations and their dimers

substrate	radical	^{31}P hyperfine coupling/G[a]			^{1}H hyperfine coupling/G	g-factor[a]		
		$A_{\parallel}$	$A_{\perp}$	A_{iso}		$g_{\parallel}$	$g_{\perp}$	g_{av}
PMe_3 in $FCCl_3$	PM_3^+	584	285	385	11.5	2.0019	2.008	2.0059
	$[Me_3P]_2^+$	592	458	503	3.3	—	—	—
PEt_3 in $FCCl_3$	PEt_3^+	*ca.* 550	—	—	—	—	—	—
	$[Et_3P]_2^+$	557	412	460	3.6 (12 H)	—	—	—
PBu_3 in $FCCl_3$	PB_3^+	529	247	341	27	2.0019	2.0038	2.003
PPh_3 in $FCCl_3$	PPh_3^+	455	216	295	—	—	—	—
	$[Ph_3P]_2^+$	—	376	—	—	—	—	—
PPh_3 in CCl_4	PPh_3^+	460	230	306	—	2.003	2.008	2.006
$P(OMe)_3$ in $FCCl_3$	$P(OMe)_3^+$	900	713	776	—	2.0038	2.0026	2.003
	$[(OMe)_3P]_2^+$	746	628	667	—	—	—	—
$P(OMe)_3$ in CCl_4	$P(OMe)_3^+$	1002	804	870	—	2.0049	2.004	2.0043
	$[(OMe)_3P]_2^+$	749	634	672	—	—	—	—
$P(OMe)_3$ in $FCCl_3$	$P(OMe)_3^+$ (A)	996	804	868	—	—	—	—
CCl_4 mixture	$P(OMe)_3^+$ (B)	910	722	785	—	—	—	—
$P(OEt)_3$ in $FCCl_3$	$P(OEt)_3^+$	895	702	767	—	2.0031	2.0007	2.0015
	$[(OEt)_3P]_2^+$	741	629	666	—	—	—	—
$P(OEt)_3$ in CCl_4	$[(OEt)_3P]_2^+$	739	627	664	—	—	—	—

[a] Corrected using the Breit–Rabi equation.

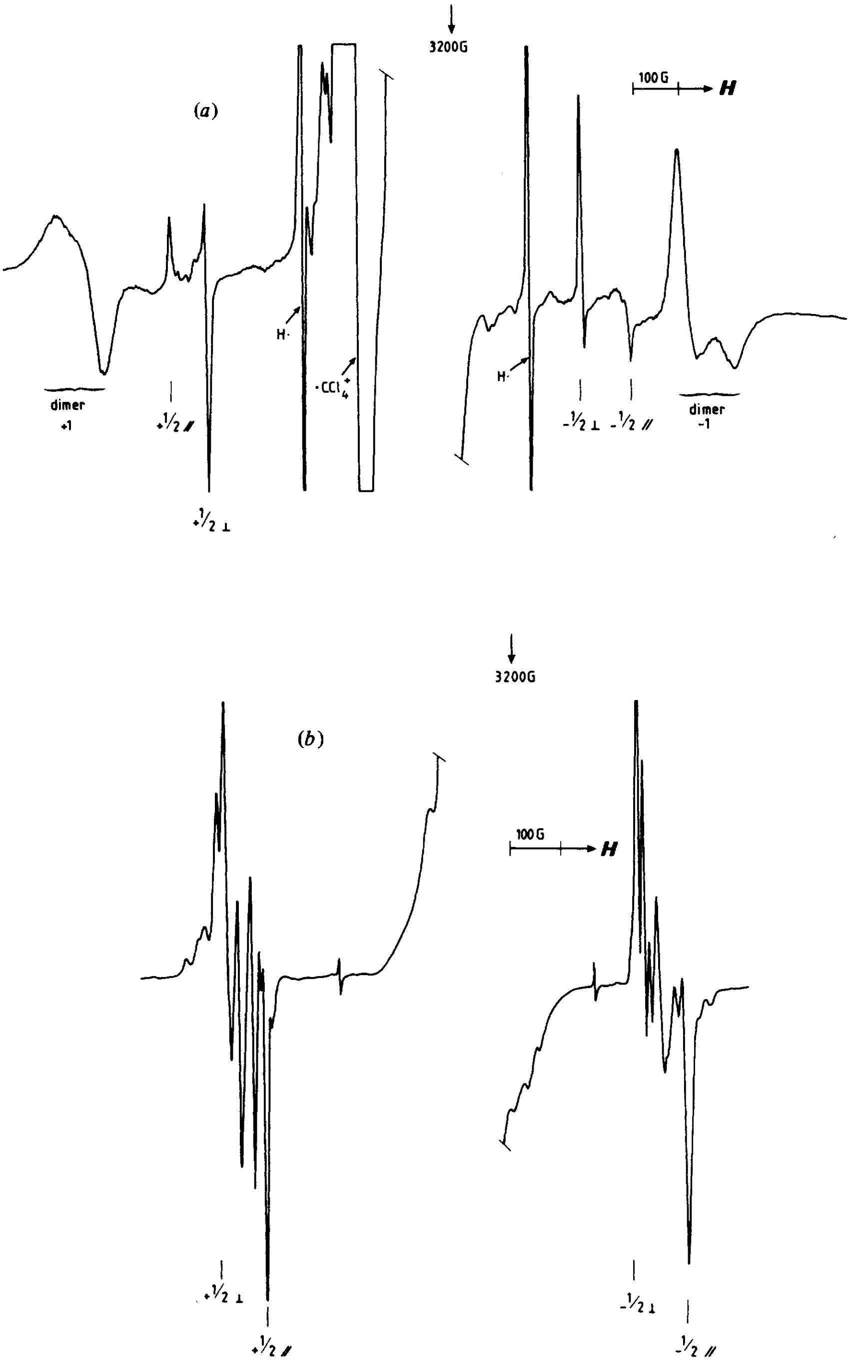


Fig. 2. For legend see opposite.

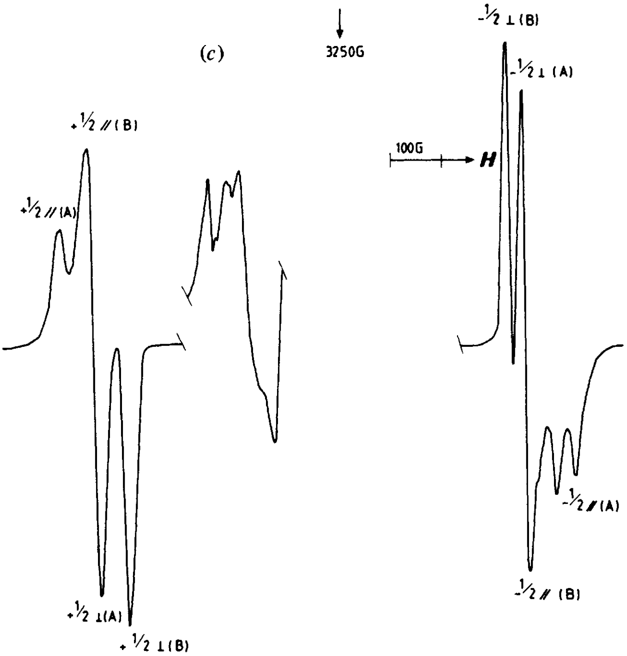
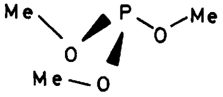
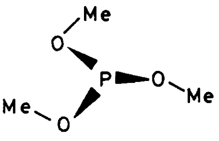


Fig. 2. First-derivative X-band e.s.r. spectra for dilute solutions of P(OMe)$_3$ after exposure to ^{60}Co γ-rays at 77 K showing features assigned to $\cdot$P(OMe)$_3^+$ cations in (*a*) CCl$_4$ (species A), (*b*) CFCl$_3$ (species B) and (*c*) a mixture of CCl$_4$ and CFCl$_3$ (20% CCl$_4$). In (*b*) the extra lines discussed in the text can be seen. The very weak outermost lines are due to the species formed in CCl$_4$. In (*c*) the outer lines are close to species A and the inner to species B.



(I)



(II)

that mixtures seem to favour the former structure. For the triethoxy derivative only the freon structure (II) is observed in both solvents. This is the sterically favoured structure and we conclude that the bulky ethyl groups are unable to adopt the more restricted structure (I). Analysis of the approximate spin densities derived from the hyperfine data (table 2) show that delocalization onto oxygen is *ca.* 17% for the freon species and only *ca.* 12% for the CCl$_4$ species. This accords with the proposed structures in that pseudo-π delocalization is impossible for structure (I) but can occur for structure (II).

EFFECT OF METHYLATION

The series $\cdot$PO$_3^{2-}$, MeO$\dot{\text{P}}$O$_2^-$, (MeO)$_2\dot{\text{P}}$O and $\cdot$P(OMe)$_3^+$ is now complete. The results are indicated in fig. 4, which shows how $A_{\text{iso}}(^{31}\text{P})$, and hence the 3*s* character of the SOMO, increases as methylation increases. Data assigned to HOPO$_2^-$[22] and $\cdot$P(OH)$_3^+$[23] are included. The value of *ca.* 450 G indicated for PO$_3^{2-}$ (α) has been extrapolated from

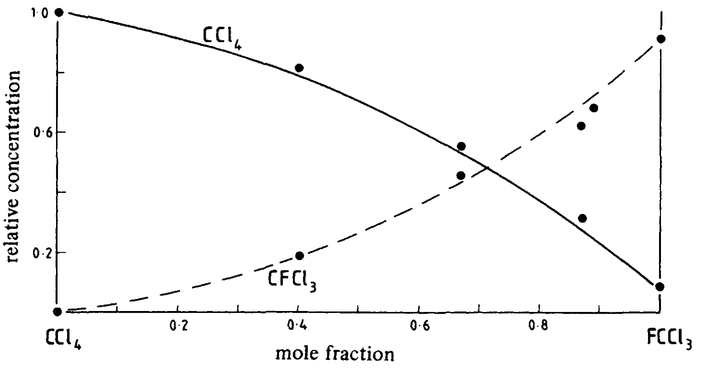


Fig. 3. Trend in the ratio of the concentration of the two major forms of $\cdot P(OMe)_3^+$ radicals as a function of mole fraction of $CFCl_3$ in CCl_4.

Table 2. E.s.r. parameters

radical	$2B$	a_s^2 (%)	a_p^2 (%)	λ^2
PMe_3^+	199	10	99	9.9
$[PMe_3]_2^+$	89	13	44	3.4
$[PEt_3]_2^+$	97	12	48	4
PPh_3^+	160	8	79	9.9
$P(OMe)_3^+$	124	19	62	3.3
$P(OMe)_3^+$	132	24	65	2.7
$[P(OMe)_3]_2^+$	79	18	39	2.2
$P(OEt)_3^+$	128	21	63	3
$SiMe_3\cdot$[a]		15	85	5.7
$\cdot AlH_3^-$[b]		15.6	70	4.5
PBu_3^+	188	9	93	10

[a] A. Begum, J. H. Sharp and M. C. R. Symons, *J. Chem. Phys.*, 1970, **53**, 3756. [b] Ref. (25).

data for a range of salt matrices, since the results span a wide range, covered by the vertical line in fig. 4. The effect of the cations is comparable with that of methylation and needs to be allowed for to give a reasonable datum for 'free' PO_3^{2-} ions.[23] The effect of strong hydrogen bonding is similar, as can be seen for $\cdot PO_3^{2-}$ in water (β) and for $HO\dot{P}O_2^-$ in water. This accounts for the difference between the results for $HO\dot{P}O_2^-$ and $MeO\dot{P}O_2^-$. The trend suggests that the result for $\cdot P(OMe)_3^+$ in freon is more in line with the other centres that that for $\cdot P(OMe)_3^+$ in CCl_4. This accords with our conformational argument, given above, and the results for $\cdot P(OEt)_3^+$ which fit well onto the correlating line.

COMPARISON WITH SILICON AND ALUMINIUM CENTRES

Recent results for $\cdot AlH_3^-$[24, 25] make it clear that the trend in estimated 3*s* character for the SOMO in the isoelectronic series $\cdot AlH_3^-$, $\cdot SiH_3$ and $\cdot PH_3^+$ is negligibly small. Two different sets of data for A_0, the calculated atomic value for unit *s*-orbital population,[26, 27] give (15.6; 15.0; 14.2) % and (11.0; 11.1; 11.0) %, respectively. Since

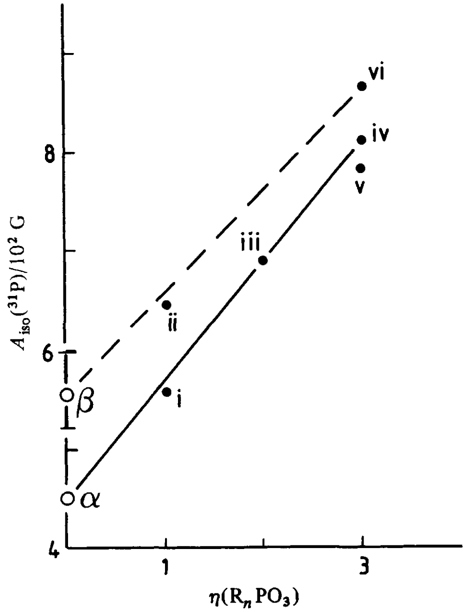


Fig. 4. Effect of methylation on the isotropic ^{31}P hyperfine coupling for $\cdot PO_3^{2-}$ radicals; *n* is the number of methyl groups bonded to oxygen. A range of data for $\cdot PO_3^{2-}$ radicals in various crystals are covered by the vertical line. The point marked α is a value extrapolated to give an expectation value for a 'free' $\cdot PO_3^{2-}$ ion; that marked β is for PO_3^{2-} in water. (i) $(MeO)\dot{P}O_2^-$, (ii) $HO\dot{P}O_2^-$, (iii) $(MeO)_2\dot{P}O$, (iv) $\cdot P(OH)_3^+$, (v) $\cdot P(OMe)_3^+$ in $CFCl_3$ and (vi) $\cdot P(OMe)_3^+$ in CCl_4. The two lines simply show the outer limits of the correlations.

the numerical values for A_{iso} (^1H) for $\cdot AlH_3^-$ and $\cdot SiH_3$ are comparable, it seems that the structures for these species are remarkably constant, in contrast with expectation based on Pauling's electronegativity theory.[26, 28, 29]

However, the results for $\cdot SiMe_3$ and $\cdot PMe_3^+$ display the expected trend on going from silicon to phosphorus (table 2), with a sharp fall in estimated 3*s* character together with an increase in $|A|(^1H)$ (from 6.3 to 11.5 G)]. The *p*:*s* ratio estimated from A_{iso} and $2B$ changes from *ca* 6.5 for $\cdot PH_3^+$ to *ca.* 9.0 for $\cdot PMe_3^+$ indicate a flattening on methylation. In contrast, there is little change on going from $\cdot SiH_3$ to $\cdot SiMe_3$.[30] Unfortunately, it seems probable that early results assigned to $\cdot AlR_3^-$ radicals[2] should have been assigned to the dimer anions.[25] We suggest that the differences in the behaviour of the silicon and phosphorus radicals can be understood in terms of a positive-charge-induced flattening of these pyramidal radicals on methylation. It is clear[31, 32] that, for carbon-centred radicals, hyperconjugation involving C—H orbitals increases as the positive charge increases. Thus electron donation *via* σ–π overlap (hyperconjugation) should be greater for $\cdot PMe_3^+$ than for $\cdot SiMe_3$, in accord with the marked increase in $A(^1H)$. It seems that this is accompanied, and possibly facilitated, by a flattening at the phosphorus centre. In the light of the hydride results it seems that this flattening is largely caused by enhanced σ–π delocalization rather than by electronegativity changes.

However, the increases in 3*s* character and the *p*:*s* ratio on going from $\cdot PH_3^+$ to $\cdot PO_3^{2-}$ and from $\cdot PO_3^{2-}$ to $\cdot P(OMe)_3^+$ are most readily understandable in terms of an increase in electronegativity of the ligands.[28, 29] On going from $\cdot PH_3^+$ to $\cdot PO_3^{2-}$ there is

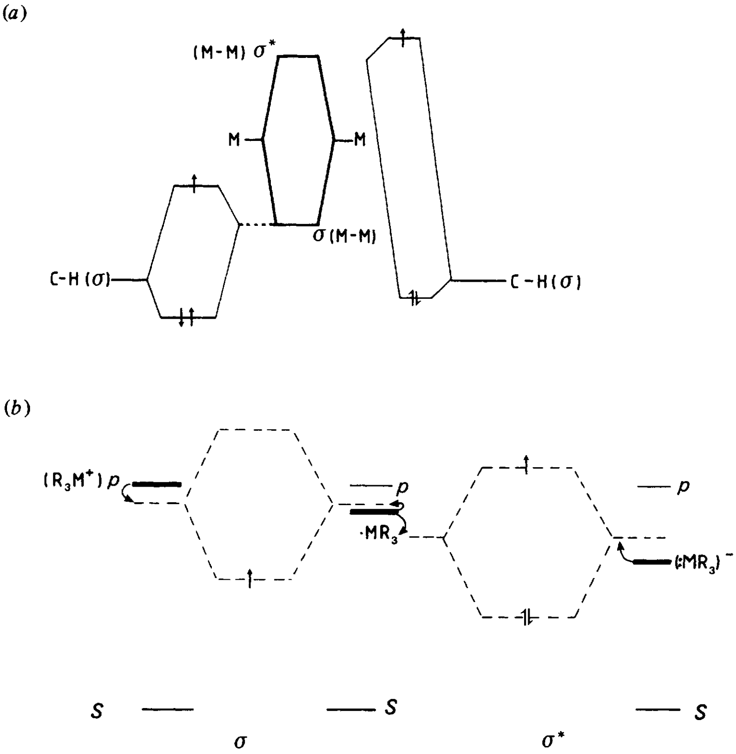


Fig. 5. Orbital-energy diagram for σ and σ* dimers.

the onset of pseudo-π delocalization in addition to σ delocalization, but on going from $\cdot PO_3^{2-}$ to $\cdot P(OMe)_3^+$ pseudo-π delocalization is expected to be reduced, as is indicated by the reduction in delocalization onto oxygen. We conclude that at this level of discussion there seems to be no clear-cut single explanation for all the observed trends and, in particular, that the apparently successful electronegativity rule[26] is by no means universally applicable.

DIMER CATIONS

We have previously called attention to e.s.r. results which indicate that there is a marked confinement of the SOMO to the localized σ* orbital in σ* radicals, such as $(R_3P \dot{-} PR_3)^+$, relative to the parent cations (*e.g.* $R_3P\cdot^+$).[14, 33, 34] In the present cases this concept is well illustrated by the ^{31}P hyperfine coupling constants and also by the ^1H coupling, which falls from 11.5 G for $\cdot PMe_3^+$ to *ca.* 3.3 G for $(Me_3P \dot{-} PMe_3)_2^+$ (table 1).

The most satisfactory explanation for this 'confinement' theory is the raising of the orbital energy of the SOMO on forming the σ bond. This is shown qualitatively in fig. 5(*a*) for $\cdot PMe_3^+$ and its dimer. The increased disparity in energy between the CH σ orbitals and the σ* orbital is thought to be responsible in this case. Similarly, for $\cdot P(OMe)_3^+$ and its dimer cation the increased difference relative to the 2*p* oxygen orbitals is thought to be responsible.

As stressed by Wang and Williams,[35] this is not true for dimer radicals with a σ SOMO. Thus, on going from $Me_3Si\cdot$ to $(Me_3Si\cdot SiMe)_3^+$ the proton hyperfine coupling only falls slightly from 6.28 to *ca.* 5.6.[35] This is readily understood in terms of the bonding scheme of fig. 5(*a*), since there is now a lowering of the SOMO so that its energy more closely matches that of the C—H orbitals.

Unfortunately, the change in $A(^{29}Si)$ on going from $\cdot SiMe_3$ to the dimer cation is unknown. However, it is known for the isostructural pair of cations $\cdot SnMe_3$[36] and $(Me_3Sn\cdot SnMe_3)^+$.[37] In this case there is a marked fall in $A_{iso}(^{117/119}Sn)$, suggesting a flattening at the metal centres. In contrast the ^{31}P data for $(R_3P\dot{-}PR_3)^+$ cations indicate increased bending for the $\cdot PMe_3^+ \rightarrow (Me_3P\dot{-}PMe_3)^+$ change (table 2). These trends, which are readily understandable in terms of the structures of the separate fragments [fig. 5(*b*)], tend to counteract the effect indicated in fig. 5(*a*), but presumably this is not sufficient to reverse the observed trends. It may be that, for the methyl derivatives considered here, the increase in hyperconjugative electron release expected on going from neutral $\cdot SiMe_3$ to the positively charged dimer plays some part in the observed trend. This latter concept has, however, received no support from the calculations of Glidewell,[38] who seems to support the σ^* 'confinement' theory, although this is incorrectly attributed to Wang and Williams, unless we have seriously misinterpreted their hypothesis[35] which is based on Whiffen's explanation of the structure of cyclohexadienyl radicals.[39]

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