

E.S.R. Spectra for the Radical Cations of $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ generated by Ionising Radiation: Evidence for a Bent P–P Bond

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The radical cation, $\text{Ph}_2\text{PCH}_2\text{PPh}_2^{+\cdot}$, has a SOMO which is localised on one phosphorus centre; however, one form of the $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2^{+\cdot}$ cation has two equivalent phosphorus nuclei, the unusual form of the e.s.r. spectrum suggesting that the directions of the s–p hybrid orbitals on each phosphorus atom subtend an angle of about 90° .

Exposure of the title compounds as dilute (1 : 1000) solutions in CFCl_3 to ^{60}Co γ -rays at 77 K gave species whose e.s.r. spectra show doublet splittings, indicating the presence of strongly coupled ^{31}P nuclei. This procedure is expected to yield only the radical cations of the substrates (or their unimolecular decomposition products),¹ and we are confident that these features can be assigned to the parent cations. Central features (not shown) can probably be ascribed to the alternative structure, in which the 'hole' is confined to one or more phenyl groups. These features are poorly defined and we cannot make firm identifications.

For $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, the outer regions of the spectrum show the presence of only one species, the parallel and perpendicular hyperfine coupling constants, assigned to one strongly coupled ^{31}P nucleus, being characteristic of $\text{R}_3\text{P}^{+\cdot}$ cations.² Each feature is further split into doublets with $A \approx 20$ G ($G = 10^{-4}$ T). This species is probably the parent cation ($\text{Ph}_2\text{PCH}_2\text{PPh}_2^{+\cdot}$).

A similar centre was also detected in $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ when irradiated under these conditions, together with a

species with greater overall splitting (Figure 1). We suggest that, in this case, the isolated 'centre', $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2^{+\cdot}$, is formed together with the cyclic dimer-cation (Figure 2). The $\text{R}_3\text{P}^{+\cdot}$ centre again shows a single extra doublet splitting ($A \approx 20$ G). This splitting could be due to the second ^{31}P nucleus, or to one of the methylene protons. However, a very similar doublet splitting of *ca.* 30 G was seen for $\text{Ph}_3\text{P}^{+\cdot}$ radicals in CFCl_3 .² This was not seen when CCl_4 was used and hence was assigned to ^{19}F coupling. Similar small doublet features have been observed in the e.s.r. spectra for several other radical-cations in CFCl_3 .³ We suggest, therefore, that the present coupling is also caused by interaction with ^{19}F .

On annealing, there were no major changes in the spectra for the single phosphorus centres. It is interesting that, for $\text{Ph}_2\text{PCH}_2\text{PPh}_2^{+\cdot}$ cations especially, there is no through-bond

delocalisation such as that found for $\text{R}\overset{\cdot}{\text{O}}\overset{+}{\text{C}}\text{H}_2\overset{\cdot}{\text{O}}$ cations. These are clearly delocalised units, the very large ^1H coupling to two equivalent protons showing that the C–H bonds are strongly involved in the SOMO.⁴ In the present case, we

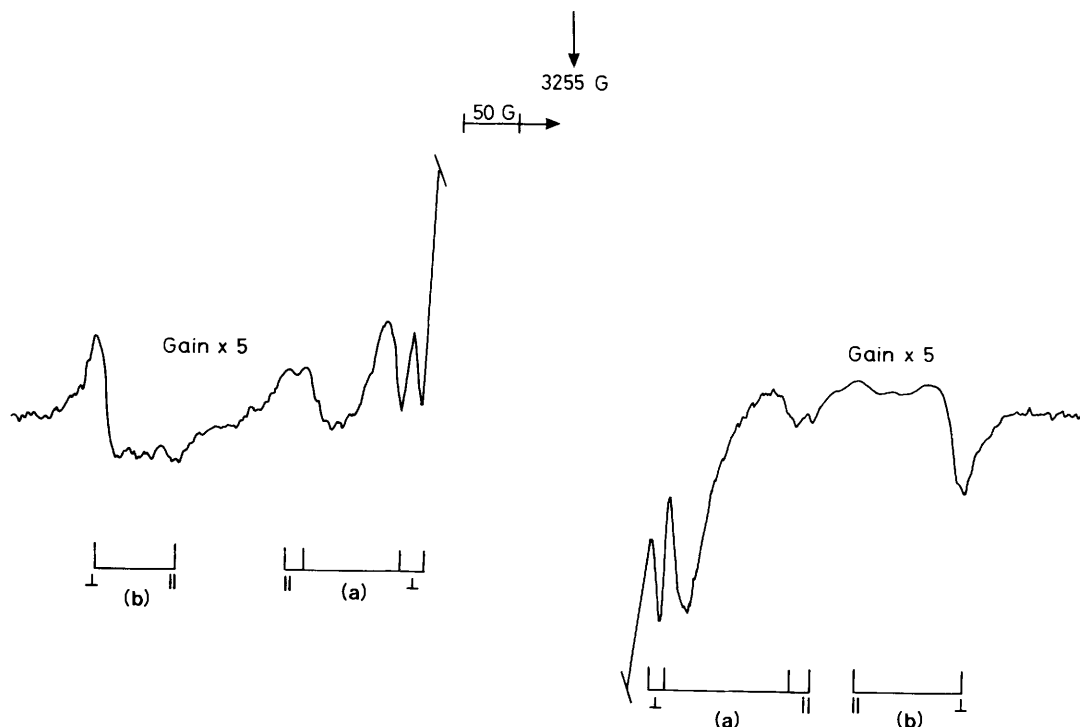


Figure 1. First derivative e.s.r. spectrum from a dilute solution of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Ph}_2$ in CFCl_3 after exposure to ^{60}Co γ -rays at 77 K, showing inner features (a) assigned to the $M_I = 1/2$ hyperfine components for $\text{RCH}_2\text{PPh}_2^+$ cations and outer features (b) assigned to the $M_I = \pm 1$ features for the cyclic cation (Figure 2) (central radical features have been omitted for clarity).

Table 1. E.s.r. Parameters for various phosphorus-centred radical cations

Cation	Hyperfine coupling/ $\text{G}^{\text{a,b}}$			g -values	
	A_{\parallel}	A_{\perp}	A_{iso}	g_{\parallel}	g_{\perp}
$\text{Ph}_3\text{P}^{+\text{c}}$	460	230	306	2.003	2.008
$\text{Ph}_2\text{PCH}_2+\dot{\text{P}}\text{Ph}_2^{\text{d}}$	450	250	317	2.002	2.007
$\text{Ph}_2\text{PCH}_2\text{CH}_2+\dot{\text{P}}\text{Ph}_2$	455	250	318	2.002	2.007
$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2^{\text{e}}$ (316)	(395)	369	2.002	2.007	
f	474	316	2.002	2.007	
$\text{Me}_3\text{P}^+\text{PMe}_3^+$	592	458	503		

^a $1\text{G} = 10^{-4}\text{ T}$. ^b Corrected to second order. ^c Ref. 2. ^d Second doublet splitting *ca.* 22 G. ^e Apparent values taken from the spectrum. ^f Corrected values.

suggest either that the angular distortion (flattening) which occurs on electron-loss fixes the SOMO on one side of the molecule, or that steric constraints involving the large phenyl groups make one Ph_2P unit twist relative to the other so that overlap is not significant. This requires that direct σ -delocalisation is not important.

The most striking result is that the experimental $A_{\perp} > A_{\parallel}$ (Figure 1). This is most unusual. Intermolecular dimer cations, $\text{R}_3\text{P}^+\text{PR}_3^+$, are known,^{2,5} but the $M_I = \pm 1$ lines have the expected form, with A_{\parallel} (A_z) $>$ A_{\perp} ($A_{x,y}$). Rapid rotation of such a dimer about x or y can generate a spectrum of the type observed, but this would be unprecedented for such a large cation in CFCl_3 at 77 K. Also, there was no relative enhancement of the outer doublet features on increasing the concentration, as is required were the species formed by a bimolecular reaction. We prefer to suggest that the P-P

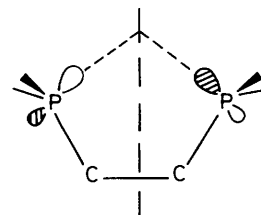


Figure 2

interaction occurs as indicated in Figure 2. Here, the principal axes for the two s - p hybrids on phosphorus, which largely comprise the postulated SOMO, subtend an angle of *ca.* 90° . In such a case, the axis normal to the ring plane (z) is a true perpendicular axis and corresponds to the A_{min} value (*i.e.* to $A_{\parallel}^{\text{exp}}$ in Figure 1). Since the A_{max} feature appears to include both the A_x and A_y (exp) components, we require that $A_x \approx A_y$. These can thus be set equal to the average of the true A_{\parallel} and A_{\perp} values and, since A_{\perp} is known (A_z), we can calculate an approximate value for the true A_{\parallel} .⁶

The spin-density ($3s + 3p$) on each phosphorus atom (*ca.* 50%) and the $p:s$ ratios (*ca.* 4.8) are comparable with those for normal dimers,² which strongly support our assignment. These were calculated from the A_{iso} (^{31}P) and $2B(^{31}\text{P})$ values obtained from the 'true' A_{\parallel} and A_{\perp} data, together with the couplings calculated for unit population of the $3s$ and $3p$ orbitals on phosphorus.⁷ We do not, of course, expect a perfect correspondence, since the bonding in Figure 1 must be much weaker than in an unconstrained dimer. Sulphur analogues of this dimer have been studied optically by Asmus and co-workers, who measured the $\sigma \rightarrow \sigma^*$ transition, the frequency of which is a fair measure of the bond strength. The values for constrained cyclic dimers are, indeed, of considerably lower energy than those for the unconstrained dimers.⁸ A

study of trends in g -values suggested that weak S \pm S bonding occurs in the radical cations of 1,3-dithiacyclopentane and 1,3-dithiacyclohexane, but, in the absence of ^{33}S features, the degree of orbital alignment could not be measured.⁹

We conclude that the SOMO for $(\text{Ph}_2\text{PCH}_2\text{PPh}_2^{+\cdot})$ radical cations is largely confined to one phosphorus atom. In contrast, the cation of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ can exist in two forms: localised and delocalised (Figure 2). In the delocalised structure, the SOMO comprises two s-p hybrid orbitals which subtend an angle close to 90° . This seems to be a very direct example of a strongly bent σ -bond.

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