

E.S.R. Evidence for the σ -State of a Diphosphene Radical Cation

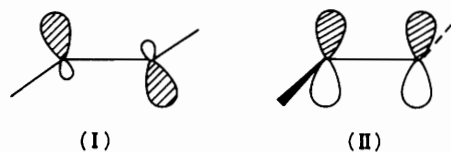
Christopher J. Rhodest

School of Chemistry, Thames Polytechnic, Wellington St., Woolwich, London SE18 6PF, U.K.

E.s.r. data indicate that the diphosphene radical cation, $(2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2)_2\text{P}_2^{+\cdot}$, isolated in a solid Freon matrix at 77 K, exists in the σ electronic state.

In recent years, considerable efforts have been made to synthesise and obtain spectroscopic data for compounds containing multiple bonds involving elements beyond the first row of the periodic table. The most widely used approach is to encumber the multiple bond with bulky substituents, thus providing kinetic stabilisation.

Among the many interesting compounds so obtained are those containing P=P double bonds: $(2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2)_2\text{P}_2$ ¹ and $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{P}_2$.² The electrochemical properties of these diphosphenes have been studied,^{3,4} and it was found that the radical anions were sufficiently stable in solution for their



e.s.r. spectra to be recorded;³⁻⁵ however, similar attempts to observe the corresponding radical cations by oxidation in the liquid phase were apparently unsuccessful.^{3,4}

Two possible structures might be expected for a diphosphene cation:⁶ the σ -state, formed by ionisation of the 'out-of-phase' phosphorus lone-pair combination (n_-) (I); or the π -state (II), resulting from the loss of a single P=P π -electron.

[†] *Present address:* Department of Chemistry, Queen Mary College, University of London, Mile End Road, London E1 4NS, U.K.

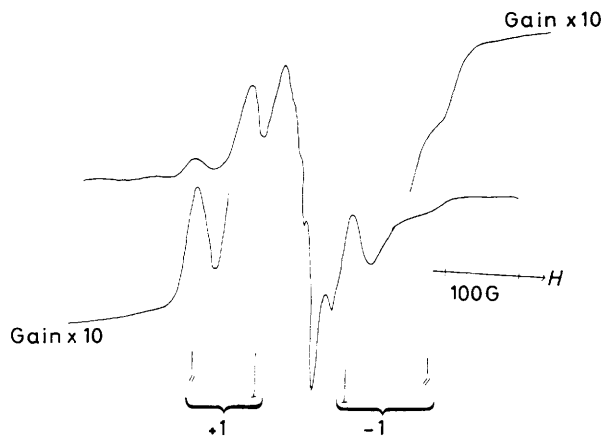


Figure 1. X-Band e.s.r. spectrum recorded following γ -irradiation of $(2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2)\text{-P=P-(C}_6\text{H}_2\text{Bu}^t_3\text{-2,4,6)}$ as a dilute solution in $\text{CF}_2\text{ClCFCl}_2$ at 77 K, containing features assigned to the parent σ -radical cation ($1\text{ G} = 10^{-4}\text{ T}$).

In view of the intrinsic interest in determining the electronic state of a diphosphene radical cation, we decided to apply the well established Freon matrix technique^{7,8} to observe the solid state e.s.r. spectrum of the $(2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2)_2\text{P}_2^{+\cdot}$ cation. This procedure gives rise to only the parent substrate radical cations or to radicals formed by unimolecular breakdown of the cations.

Following γ -irradiation of the parent diaryl-diphosphene as a dilute solution in $\text{CF}_2\text{ClCFCl}_2$ at 77 K, spectra such as that shown in Figure 1 were recorded. The spectrum shows an intense central feature which we suggest is partly due to π -radical cations resulting from ionisation of an aromatic group. Additionally, there are outer (parallel) features separated by 356 G, which correspond to a value for A_{\parallel} of 178 G (correct to second order). There are also features present which can be assigned to perpendicular components, giving $A_{\perp} = 63\text{ G}$. This leads to the following ^{31}P hyperfine parameters: $A_{\parallel} = 178$, $A_{\perp} = 63$, $A_{\text{iso}} = 101$, $2B = 77\text{ G}$, from which 3s and 3p orbital populations of 0.028 and 0.383 may be derived,⁹ showing that 82% of the spin-density is centred on the phosphorus atoms. The p/s ratio of 13.7 is lower than that normally observed for π -radicals (ca. 20–30), and since the isotropic coupling is nearly twice that measured for the π -radical anion^{3,5} in the liquid phase, we assign the σ -structure to the radical cation.

From the p/s ratio, we can obtain an estimate of the C–P–P bond angles of ca. 150° ;‡ it appears that substantial opening of

these bond angles occurs on ionisation since X-ray data show that the corresponding C–P–P angles in the parent compound are 103° .¹⁰ If, as seems likely, the phenyl groups in the cation are oriented at ca. 90° to the P=P plane, as they are in the parent molecule,¹⁰ then the reduction in the total spin-density on the P=P unit (18%) may be partly explained in terms of delocalisation onto the aromatic substituents. Such delocalisation might be expected to increase the C–P–P bond angles to some extent, as partial double bond character is introduced to the C–P bonds.

There is some controversy regarding the assignment of the lowest energy band in the photoelectron spectra of diphosphenes. Some workers propose that it is due to ionisation from the P=P π -orbital,¹¹ whereas others favour ionisation from the n_{p} orbital,¹⁰ leading to π - and σ -cations, respectively. The e.s.r. result may therefore be taken to support the latter assignment; however, the e.s.r. data refer to 'relaxed' cations, whereas the photoelectron results refer to essentially 'vertical' species. We call attention to our recent e.s.r. studies^{12,13} of the analogous azoalkane radical cations ($\text{R-N=N-R}^{+\cdot}$) which exist as the π -state in a solid Freon matrix, despite photoelectron evidence¹⁴ that the first ionisation takes place from the n_{p} -orbital.

I thank Professor M. C. R. Symons, Leicester University, for access to e.s.r. facilities and Mr. D. Carmichael for providing the sample of the diaryl-diphosphene.

Received, 4th January 1989; Com. 9/00094A

References

- M. Yoshifuji, M. Shima, and N. Inamoto, *J. Am. Chem. Soc.*, 1983, **103**, 4587.
- J. Jaud, C. Couret, and J. Escudie, *J. Organomet. Chem.*, 1981, **249**, C25.
- A. J. Bard, A. H. Cowley, J. E. Kilduff, J. K. Leland, N. C. Norman, M. Pakulski, and G. A. Heath, *J. Chem. Soc., Dalton Trans.*, 1987, 249.
- M. Culcasi, G. Gronchi, J. Escudie, C. Couret, L. Pujol, and P. Tordo, *J. Am. Chem. Soc.*, 1986, **108**, 3130.
- B. Çetinkaya, A. Hudson, M. F. Lappert, and H. Goldwhite, *J. Chem. Soc., Chem. Commun.*, 1982, 609.
- V. Galesso, *Chem. Phys.*, 1984, **83**, 407.
- M. Shiotani, *Mag. Reson. Rev.*, 1987, **12**, 333.
- M. C. R. Symons, *Chem. Soc. Rev.*, 1984, **13**, 393.
- M. C. R. Symons, in 'Chemical and Biochemical Aspects of Electron-Spin Resonance Spectroscopy,' ed. M. C. R. Symons, Van Nostrand-Reinhold, New York, 1978.
- D. Gonbeau and G. Pfister-Guillouzo, *J. Electron Spectrosc.*, 1984, **33**, 279.
- B. Çetinkaya, M. F. Lappert, J. G. Stamper, and R. J. Suffolk, *J. Electron Spectrosc.*, 1983, **32**, 133.
- C. J. Rhodes and P. W. F. Louwrier, *J. Chem. Res. (S)*, 1988, 38.
- C. J. Rhodes, *J. Chem. Soc., Faraday Trans. 1*, 1988, 3215.
- K. N. Houk, Y.-M. Chang, and P. S. Engel, *J. Am. Chem. Soc.*, 1975, **97**, 1824.

‡ The method, outlined in ref. 9, assumes complete orbital following and that all of the isotropic component arises directly from the s-electron spin-density in the singly occupied s/p hybridised orbital. Since in reality some of this component will stem from spin-polarisation of the other electrons on the atom in question, then a further uncertainty exists.