Bonding in Phosphonitrilic Chloride Trimer: Electron Spin Resonance Evidence for the Radical Anion

By Shuddhodan P. Mishra and Martyn C. R. Symons*

(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary The e.s.r. spectrum for γ-irradiated hexachlorocyclotriphosphazene is dominated by features assigned to the anion having the unpaired electron entirely confined to a single phosphorus and two chlorine atoms.

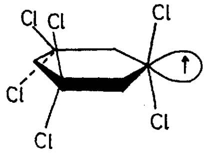
The nature of the bonding in phosphonitrilic compounds is a problem of long standing.[1] However, there is agreement that for the planar cyclic compounds a pseudo-aromatic π-system is of significance, involving $3d$, $4s$, and $4p$ orbitals on phosphorus. Recently, the hexaphenyl trimer has been electrochemically reduced, and a singlet e.s.r. spectrum assigned to the radical anion. The fact that no hyperfine structure was obtained was taken as evidence for extensive electron delocalisation in the π-system or for rapid electron exchange.[2]

TABLE. *E.s.r. parameters assigned to the anion of hexachlorocyclotriphosphazene and related compounds*

Radical	Isotropic hyperfine coupling constants ^{31}P (G)	 ^{35}Cl (G)[c]	3s-Character[b] on phosphorus (%)
Present ..	1290±10	52±1	35·4
PCl_4[a]	1248	52	34·2
$POCl_3^-$[a] ..	1359	67	37·3

[a] From ref. 4(c). [b] Estimated using $A^\circ(3s)^{31}P = 3640$ G (P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, 1967). [c] For the two strongly coupled chlorine atoms.

However, we have presented e.s.r. evidence against π-delocalisation in $R_2\dot{C}\text{-}\overset{+}{P}R_3$ radicals[3] and consider that the same arguments are valid for the phosphonitrilic systems. Thus, despite suggestions against such a concept,[1] we consider that these compounds are partially ionic, the adjacent opposite charges being partially neutralised by σ- rather than π-delocalisation, but being nevertheless a strong stabilising factor, responsible, for example, for the short P–N bonds of these molecules.



(I)

Experience with many four-covalent phosphorus radicals such as PF_4, PC_4, $POCl_3^-$, PO_4^{4-}, *etc.* strongly suggests that the radical anion of the title compound would have its excess electron bonded primarily to phosphorus in an orbital comprising primarily phosphorus 3*s* and 3*p* atomic orbitals.[3] Thus for the title compound we expect either a structure in which the Cl–P–Cl angle has opened considerably with the electron in an equatorial orbital, see (I), or, if the distortion is slow compared with the migration rate, the electron might jump between the three phosphorus atoms.

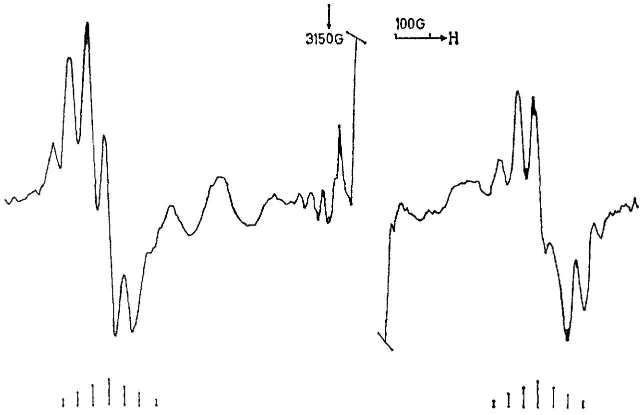


FIGURE. *First derivative X-band e.s.r. spectrum for the title compound after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to the radical anion (a large doublet splitting from coupling to ^{31}P and a septet from two equivalent chlorine atoms).*

In fact, at 77 K the former situation holds, the e.s.r. spectrum (Figure) being unambiguously that of the anion having two strongly coupled chlorine atoms, just as in PCl_4, the electron being otherwise confined to a phosphorus hybrid orbital with very large 3*s* orbital character (Table). This result seems to us to be markedly at variance with the majority of predictions for this molecule.[1]

These results suggest that those recently reported for various radical cations of 1,4-diphosphoniacyclohexa-2,5-diene salts[5] indicate that the unpaired electron is largely confined to the carbon π^*-system, there being little or no delocalisation onto phosphorus.

(*Received*, 22*nd February* 1972; *Com.* 248.)

---

[1] H. R. Allcock, *Chem. Rev.*, 1972, **72**, 315 and references therein.

[2] H. R. Allcock and W. J. Birdsall, *J. Amer. Chem. Soc.*, 1969, **91**, 7541; *Inorg. Chem.*, 1971, **10**, 2495.

[3] A. R. Lyons, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 1063.

[4] (a) J. R. Morton, *Canad. J. Phys.*, 1963, **41**, 706; (b) P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4363; (c) A. Begum and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 2065; (d) J. Higuchi, *J. Chem. Phys.*, 1969, **50**, 1001.

[5] R. D. Rieke, R. A. Copenhafer, A. M. Aguiar, M. S. Chattha, and J. C. Williams, *J.C.S. Chem. Comm.*, 1972, 1130.