Ligand-σ Phosphoranyl Radicals

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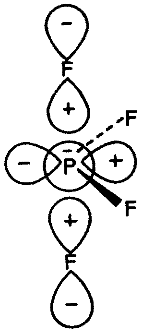
Summary Two different electronic structures of the phosphoranyl radical $[(RO)_3PNCO]^{\bullet}$, the normal trigonal-bipyramidal structure and a species in which the unpaired electron is centred on the NCO ligand in a σ-orbital, have been detected by e.s.r. spectroscopy.

The type of electronic structure adopted by a phosphoranyl radical depends upon the nature of the substituents at phosphorus. The tetrafluorophosphoranyl radical is most stable as the C_{2v} structure (**1**), and the major contributions to the singly-occupied molecular orbital (SOMO) are as shown.[1]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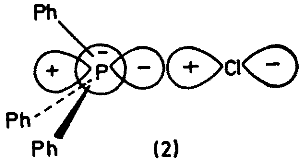
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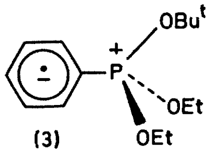
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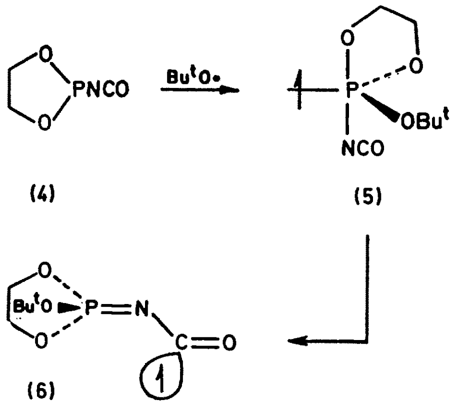
A large number of other phosphoranyl radicals adopt similar structures in which, for convenience, the unpaired electron is shown as an equatorial 'phantom' ligand and such radicals are described as being trigonal-bipyramidal (TBP). However, when the energy of one *P*-ligand σ^* orbital is significantly lower than the energies of the other three, a quasi-tetrahedral structure may be preferred.[2,3] For example, the radical (Ph$_3$PCl)• adopts the structure (**2**) and the SOMO is the σ^* P–Cl orbital.[2]

When one or more ligands possess low-energy vacant π orbitals a quasi-tetrahedral structure may again be most stable, and many phenylphosphoranyl radicals adopt structures similar to (**3**), in which the SOMO is essentially a ligand π^* orbital with the phosphorus atom lying in its nodal plane.[4,5]



We now report that addition of photochemically generated t-butoxyl radicals to the phosphorus(III) isocyanate (**4**) affords not only the e.s.r. spectrum which has been ascribed previously[6] to the TBP phosphoranyl radical (**5**), but also a signal which we assign to the isomeric radical with the ligand-σ electronic structure (**6**). The spectrum obtained during photolysis of di-t-butyl peroxide in the presence of (**4**) is shown in the Figure and e.s.r. parameters for (**5**) and (**6**), and for related radicals derived from (**4**) and (EtO)$_2$-PNCO are given in the Table.

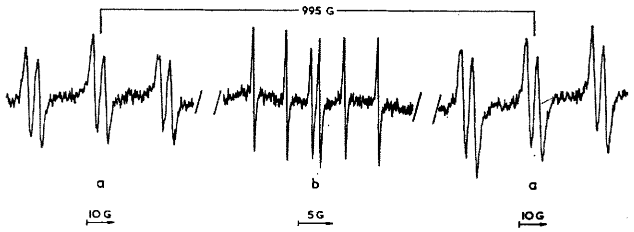
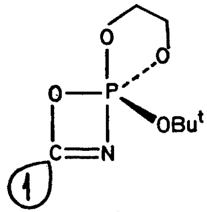


FIGURE. E.s.r. spectrum obtained during photolysis of di-t-butyl peroxide in the presence of (**4**) in cyclopropane solvent at 193 K. Lines marked a are assigned to (**5**) and those marked b are assigned to (**6**).

In support of the assignments to ligand-σ radicals, an INDO calculation[†] for [(HO)$_3$PNCO]• in the *s-trans*-conformation similar to (**6**) predicted a(P), −7·3; a(N), −1·4; and a(^{13}C), +129·4 G. The structural isomers (**7**) and (**8**) are possible alternatives to (**6**), although we would expect a(P) for the imidoyl radical (**7**) to be larger than the observed value.

However, whilst photolysis of Bu^{t}OOBu^t in the presence of EtOP(NCO)$_2$ afforded the spectrum of the TBP phosphoranyl radical Bu^{t}O(EtO)$\dot{\mathrm{P}}$(NCO)$_2$ [a(P), 1048 and a(2N), 22·2 G, and g 2·0025 at 200 K], no radical was detected which showed spectral parameters similar to those assigned to the ligand-σ phosphoranyl radicals derived from the monoisocyanates, and hence (**6**) is much more likely than (**7**) or (**8**). However, a signal showing a(1P), 41·6[‡] and a(2N), 1·6 G, and g 2·0015 at 250 K was observed, and we assign this to a ligand-σ phosphoranyl radical either in which the unpaired electron is rapidly exchanging between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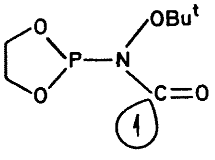
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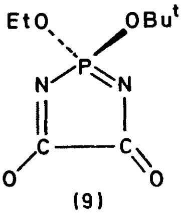
(9)

[†] INDO III calculation (A. R. Gregory, *J. Chem. Phys.*, 1974, **60**, 3713); we thank Dr. Gregory for providing us with a copy of his computer programme. Bond lengths: P–N, 1·54; N–C, 1·35; C=O, 1·20; P–O, 1·65; and O–H, 0·96 Å. Bond angles: PNC, 140; NCO, 150; and all others 109·5°.

[‡] The ^{31}P-splitting was remarkably temperature dependent: d|a(P)|/dT *ca.* −220 mG K^{-1}.

TABLE. E.s.r. parameters for phosphoranyl radicals derived from (**4**) and $\mathrm{(EtO)_2PNCO}$ in cyclopropane solvent.

	TBP structure					Ligand-σ structure				
		Hyperfine splittings/G					Hyperfine splittings/G			
Source of phosphoranyl radical[a]	T/K	a(P)[b]	a(N)	a(1H)	g-Factor[b]	T/K	a(P)	a(N)	$a(^{13}\mathrm{C})$[b,c]	g-Factor
$\mathrm{Bu^tO}\cdot$ + (**4**)	184	975·5	24·0	4·1	2·0022	223	7·7[d]	5·0[e]	136·1[f]	2·0009
$\mathrm{EtO}\cdot$ + (**4**)	185	1002·3	23·7	4·1	2·0022	227	4·4	5·6	139·5[g]	2·0010
$\mathrm{Me_3SiO}\cdot$ + (**4**)	220	1005·5	23·9	4·5	2·0023	222	8·4	5·0	135·3	2·0010
$\mathrm{(Me_3Si)_2N}\cdot$ + (**4**)		h	h	h	h	228	12·5	4·7		2·0010
$\mathrm{Bu^tO}\cdot$ + $\mathrm{(EtO)_2PNCO}$[i]	159	989·8	26·8	—	2·0023	205	5·0	5·8		2·0009
$\mathrm{EtO}\cdot$ + $\mathrm{(EtO)_2PNCO}$[i]	158	989·7	26·3	—	2·0023	171	3·7	5·8		2·0009
$\mathrm{Me_3SiO}\cdot$ + $\mathrm{(EtO)_2PNCO}$[i]	155	994[j]	26[j]	—	2·002[j]	178	6·3	5·5		2·0009
$\mathrm{(Me_3Si)_2N}\cdot$ + $\mathrm{(EtO)_2PNCO}$[i]		h	h	—	h	197	7·9	5·8		2·0010

[a] Addendum X• generated by photolysis of X–X. [b] Obtained using the Breit–Rabi equation. [c] Spectra obtained from (**4**) containing 45 atom % ^{13}C in the NCO group. [d] $\mathrm{d}|a(\mathrm{P})|/\mathrm{d}T$ −21·1 mG K^{-1}. [e] $\mathrm{d}|a(\mathrm{N})|/\mathrm{d}T$ +7·5 mG K^{-1}. [f] At 213 K. [g] At 231 K. [h] Signal too weak to analyse accurately. [i] Cyclopropane–benzene (3 : 1 by volume) solvent. [j] Weak signal.

two non-equivalent NCO groups, or in which the nitrogen atoms are equivalent, perhaps with a significant bonding interaction between carbon atoms as illustrated in the canonical structure (**9**).

Both (**5**) and (**6**) were detectable immediately upon beginning photolysis. At 170 K [(**5**)]/[(**6**)] was *ca.* 40, although [(**6**)] increased at the expense of [(**5**)] as the temperature was increased, and above *ca.* 228 K the spectrum of (**5**) was undetectable whilst that ascribed to (**6**) was strong. When the light was shuttered at 197 K, decay of the spectrum of (**5**) was first-order (k 440 s^{-1}) with respect to [(**5**)]. During the first 8 ms after interrupting photolysis [(**5**)] had decayed to *ca.* 4% of $[(\mathbf{5})]_{\mathrm{ss}}$ (the concentration during continuous photolysis), whilst [(**6**)] had decreased only to *ca.* 50% of $[(\mathbf{6})]_{\mathrm{ss}}$. We conclude that (**5**) and (**6**) are not in equilibrium under the conditions employed, and we propose that the TBP radical (**5**) is formed initially (perhaps *via* an undetected σ^* intermediate) and that (**5**) subsequently undergoes effectively-irreversible isomerisation to the ligand-σ radical (**6**).

(*Received* 12*th March* 1979; *Com.* 249.)

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[2] T. Berclaz, M. Geoffroy, and E. A. C. Lucken, *Chem. Phys. Letters*, 1975, **36**, 677.
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[6] J. W. Cooper, M. J. Parrott, and B. P. Roberts, *J.C.S. Perkin II*, 1977, 730.