

JOM 23156PC

## Preliminary Communication

### The structure of diphosphine radical cations

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(Received August 12, 1992)

#### Abstract

When  $R_2NNR_2$  molecules lose an electron to give  $(R_2NNR_2)^{+\cdot}$  radical cations, the whole unit becomes planar, with  $a(\pi_1)^2(\pi_2)^1$  configuration. However, because  $R_3P$  molecules are far more strongly pyramidal than  $R_3N$  molecules, this flattening on electron loss is less, and phosphorous centred radical cations do not achieve planarity. This is clearly so for  $(R_2PPR_2)^{+\cdot}$  centres, whose liquid and solid state spectra analysed herein in terms of two equivalent  $^{31}P$  hyperfine couplings, show *ca.* 9% 3s character. This indicates considerable bending at each phosphorous centre. Furthermore, the form of the spectra, with no *x-y* splitting of the 'perpendicular' lines, suggests that each  $^{31}P$  coupling shares a common axis. This means that a *trans* conformation is required, as expected because this relieves steric strain and favours " $\pi$ " type orbital overlap.

The structure of  $R_2N-NR_2$  molecules, depicted in Fig. 1(a), changes drastically on electron-loss to give  $(R_2NNR_2)^{+\cdot}$  radical cations [1] (Fig. 1(b)). In the parent molecule there are potentially four  $\pi$ -electrons, but these can be treated as two "lone-pairs" of electrons localised on each nitrogen, and the conformation is such that the overlap between these sp hybridised orbitals is small. Evidence from EPR spectroscopy (Table 1) shows clearly that the whole unit has become planar for  $(R_2NNR_2)^{+\cdot}$  radical-cations with maximum overlap between the two 2p orbitals. Thus the outermost orbitals are  $\pi^2;\pi^{*1}$  [1], with a significant net bonding [2].

When  $R_3N$  molecules lose an electron to give  $R_3N^{+\cdot}$ , the radical cation becomes planar, the SOMO being to the first approximation a 2p orbital on nitrogen [3]. However, when  $R_3P$  molecules lose an electron, the

$R_3P^{+\cdot}$  cations do not become planar, although there is considerable flattening [4]. Since the bond angles for phosphines are considerably smaller than those for corresponding amines this difference is not surprising, the changes in bond angles being comparable.

Similarly EPR results [5] for  $(R_2PPR_2)^{+\cdot}$  radical cations show clearly that the SOMO involves considerable 3s character on the two phosphorous atoms, showing that once again planarity is not achieved.

Coupling of the unpaired electron with two equivalent phosphorus nuclei should normally give a three line EPR spectrum. However owing to the strength of the electron-phosphorus coupling, the degeneracy of the two transitions that compose the central component of the triplet is lifted, and in the liquid phase, four line EPR spectra are observed for  $(R_2PPR_2)^{+\cdot}$  radical cations. The most intriguing feature of these spectra is the anomalous linewidth variation across the multiplet. Similar linewidth variations have also been observed [6] for analogous cations with two equivalent strongly-coupled phosphorus atoms  $(R_3PPR_3)^{+\cdot}$ , as well as in the EPR spectrum of the radical anion of bis(tris(trimethylsilyl)methyl)diphosphene [7].

Using the semiclassical density-matrix approach of magnetic relaxation we reached the tentative conclusion [8] that in solution the radical cation of the tetra-2,4,6-triethylphenyldiphosphine **3** (Table 2) exists mainly in a *gauche* conformation, with an angle  $\theta$  close to  $142^\circ$  between the directions of the phosphorus lone pairs.

The aim of the present study was to obtain solid-state spectra for  $(R_2PPR_2)^{+\cdot}$  radical cations, in the expectation that, by use of a computer simulation of the spectrum, a reasonable experimental measure of the

TABLE 1. ESR data for a range of related radicals

Radical	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	$A_{iso}$ (G)	$g_{\parallel}$	$g_{\perp}$
$(Me_2NNMe_2)^{+\cdot}$ <sup>a</sup>	27	2.5	10.7		
$(MeSSMe)^{+\cdot}$ <sup>b</sup>				2.002	2.0036 2.0017
$Me_3P^{+\cdot}$ <sup>c</sup>	584	285	385	2.0019	2.008
$(Me_3PPMe_3)^{+\cdot}$	542 <sup>d</sup> 569 <sup>a</sup>	458 439	503 482	1.992	2.012

<sup>a</sup> K. Ramani and R. Srinivasan, *Proc. Nucl. Phys. Sol. State*, 17 (1972) C199 ( $a(^1H)_{iso} = 13.2$  G). <sup>b</sup> Ref. 11. <sup>c</sup> Ref. 4. <sup>d</sup> Ref. 12b. <sup>e</sup> Ref. 12a.

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\* Dedicated to Professor Alwyn Davies, in recognition of his major contributions to the field of organometallic and radical chemistry, and to ESR spectroscopy.

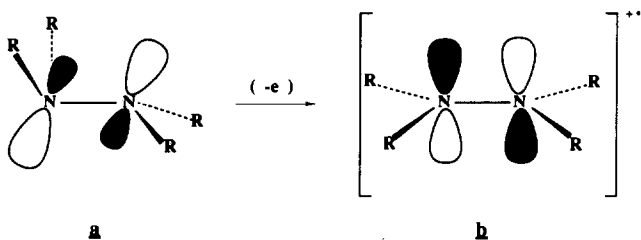


Fig. 1. SOMOs for neutral hydrazines (a) and their radical cations (b).

angle(s) between the two hyperfine directions could be obtained.

The results (Fig. 2, Table 2) show that these directions are coaxial within  $ca \pm 8^\circ$ . Thus there is no sign of any splitting of the perpendicular ( $x, y$ ) features. Computed spectra with  $\theta = 0^\circ$  agree well with the experimental spectra, showing the second order splitting of the  $|1,0\rangle$  and  $|0,0\rangle$  nuclear spin states. Calculated spectra also showed that deviations larger than  $8^\circ$  from a coaxial structure should give a resolvable  $x, y$  splitting.

On the other hand the large phosphorus splitting observed for  $(R_2PPR_2)^{+\cdot}$  radical cations, clearly indicates that for these radicals, the phosphorus centers retain a relatively large degree of bending. The  $P_{3s}$  orbital populations derived from the isotropic phosphorus splittings are close to 7%. This mean value is higher than that observed for the corresponding tri-

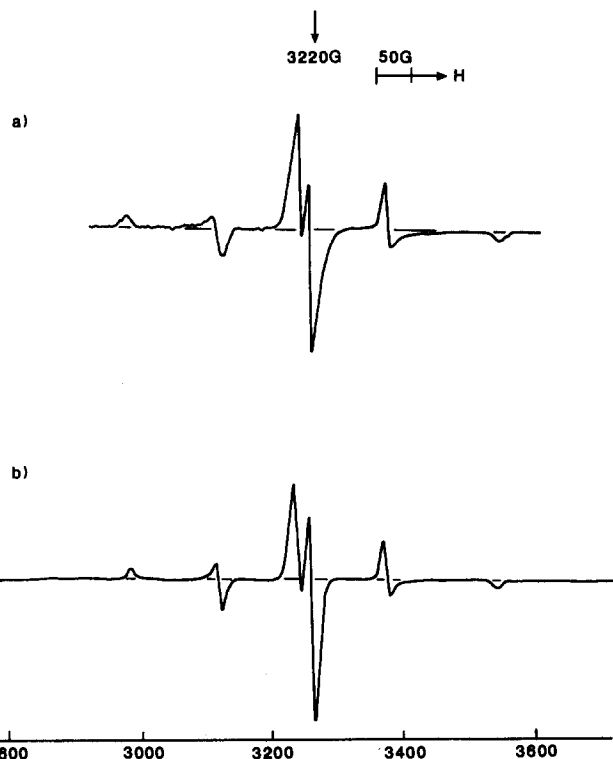


Fig. 2. (a) First derivative ESR spectrum for  $Ar_2PPAr_2$  (No. 3 in Table 2) in  $CFCl_3$  after exposure to  $^{60}\gamma$  ray at 77 K, showing features assigned to  $(Ar_2PPAr_2)^{+\cdot}$  radical cations. (b) Second order simulation using the data given in Table 2. Note the second order splitting. In this simulation, the  $^{31}P$  hyperfine parameters are assumed to have common axes.

TABLE 2. ESR data on diphosphine radical cations  $(Ar_2PPAr_2)^{+\cdot}$

Ar	$A_{P}^{iso^a}$ (G)	$A_{  }$	$A_{\perp}$	$g_{  }$	$g_{\perp}$	$g$	$T$ (K)
	171 <sup>b</sup>	279	120	2.002	2.008	2.0060 <sup>c</sup>	291
	173					2.006 <sup>d</sup>	77
	170	268	120	2.002	2.008	2.0063	290
	169					2.006	77
	175	281	125	2.002	2.008	2.0061	293
	177					2.006	77
	168	not detected <sup>e</sup>				2.0060	282
	163	not detected <sup>e</sup>				2.0060	293

<sup>a</sup> Uncorrected. <sup>b</sup> In butyronitrile solution. <sup>c</sup>  $g_{iso}$ . <sup>d</sup>  $g_{av}$ . <sup>e</sup> Only a non-assigned aromatic cation was detected.

arylphosphine radical cations (5%) [4], which are thus expected to be less bent at phosphorus. Owing to the long P–P bond distance (2.1–2.2 Å), a symmetric tetraaryldiphosphine bearing bulky aryl substituents is expected to be sterically less constrained and thus more bent at the phosphorus centers than the corresponding phosphines, and this difference persists in the radical cations.

We conclude that the structure of  $(R_2PPR_2)^{+\bullet}$  radical cations is that depicted in Fig. 3. The alternative *cis* form seems improbable in view of the large steric interactions it would involve. In contrast with  $(R_2NNR_2)^{+\bullet}$  radical cations the phosphorus centers in  $(R_2PPR_2)^{+\bullet}$  have not achieved planarity.

Our results are in good accord with the recent calculations of Clark [9] on  $P_2H_4^+$ ; but show that the localised model of Feller *et al.* [10] is incorrect. According to Clark there is considerable mixing between the SOMO ( $n^-$  in his nomenclature) and the P–P  $\sigma$  orbital that helps to stabilise the structure. His calculations suggest that this form of stabilisation is not strongly dependent on the torsional angle for  $P_2H_4^+$ ; and the calculated rotational barrier (7.9 Kcal  $M^{-1}$ ) is low. This may explain our liquid-phase results [5], which were best interpreted in terms of a twisted conformation [8].

The electronic structure of  $(R_2PPR_2)^{+\bullet}$ ; contrasts with that found for the isoelectronic sulphur derivative [11]  $(RSSR)^{+\bullet}$ . In this case there is no constraint working against a pure  $(\pi)^2$ ,  $(\pi^*)^1$  configuration which is assumed to occur. However the presence of extra “lone-pairs” type orbitals lowers the symmetry and orbital mixing giving rise to large *g*-shifts (Table 1).

Another interesting comparison is with the  $\sigma^*$  dimer species  $(R_3PPR_3)^{+\bullet}$  [12]. In these cases the two  $^{31}P$  hyperfine matrices are again coaxial, but the  $^{31}P$  isotropic hyperfine coupling is very much greater than for the  $(R_2PPR_2)^{+\bullet}$  species, and there is an increase relative to the results for the monomer cations,  $R_3P^+$ , though the spin density on phosphorus is reduced by a factor of *ca* 2. (For example,  $A_{iso}$  for each  $^{31}P$  for  $(Me_3PPMe_3)^{+\bullet}$  is *ca.* 500 G, whereas that for  $Me_3P^+$  is 385 G). Thus, in these  $\sigma^*$  3-electron centres the

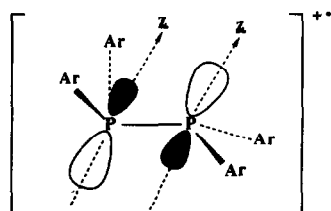


Fig. 3. Proposed SOMO for  $(Ar_2PPAr_2)^{+\bullet}$  radical cations.

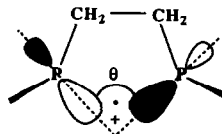


Fig. 4. SOMO for radical cations derived from 1,2-bis(diphenylphosphino)ethane [13].

influence of the two  $\sigma$ -bonding electrons strongly governs the degree of orbital hybridisation by enhancing *s*-admixture. In contrast, the two bonding electrons for  $(R_2PPR_2)^{+\bullet}$  species influence the hybridisation in the other direction, favoring *p*-admixture.

Interesting comparison can also be made with the cyclic radical cation obtained by  $\gamma$  irradiation of 1,2-bis(diphenylphosphino)ethane [13]  $(Ph_2PCH_2CH_2PPh_2)^{+\bullet}$  (Fig. 4). In this case, the ESR spectrum again suggested axial symmetry, but the apparent perpendicular splitting was greater than the parallel splitting. The best way to account for this unusual situation was to postulate a “bent”  $\sigma$ -bond as indicated. The fact that the *x* and *y* components of the hyperfine coupling coincide requires that  $\theta = 90^\circ$ . This contrasts strongly with the situation for the  $(R_2PPR_2)^{+\bullet}$  radical cations, in which the two phosphorus orbitals are parallel or nearly so.

Finally, we have been able, in the case of the  $(Et)_6$  derivative, **3**, to obtain a good solid-state spectrum after generating the radical cation in fluid solution [4] and freezing, using a solvent system (butyronitrile) that glassifies. The spectrum was identical to that shown, in Fig. 2, obtained by  $\gamma$  radiolysis.

## References

- 1 S. F. Nelsen, *Acc. Chem. Res.* **14** (1981) 131; S. F. Nelsen, S. C. Blackstock, M. P. Yumibe, T. B. Frifo, J. E. Carpenter and F. Weinhold, *J. Am. Chem. Soc.*, **107** (1985) 143.
- 2 S. F. Nelsen, G. T. Cunkle, D. H. Evans and T. Clark, *J. Am. Chem. Soc.*, **105** (1983) 5928.
- 3 Y. L. Chow, W. C. Danen, S. F. Nelsen and D. Rosenblatt, *Chem. Rev.*, **78** (1978) 243.
- 4 A. Begum, A. R. Lyons and M. C. R. Symons, *J. Chem. Soc. A*, (1971) 2290; P. Tordo, in F. R. Hartley (ed.), *The Chemistry of Organophosphorus Compounds*, Vol. 1, J. Wiley and Sons, New York, 1990, p. 187; T. Berclaz and M. Geoffroy, *Mol. Phys.*, **30** (1975) 549; M. Culcasi, Y. Berchadsky, G. Gronchi and P. Tordo, *J. Org. Chem.*, **56** (1991) 3537.
- 5 M. Culcasi, G. Gronchi and P. Tordo, *J. Am. Chem. Soc.*, **107** (1985) 7191.
- 6 W. B. Gara and B. P. Roberts, *J. Chem. Soc., Perkins Trans.*, **2** (1978) 150.
- 7 M. Culcasi, G. Gronchi, J. Escudié, C. Couret, L. Pujol and P. Tordo, *J. Am. Chem. Soc.*, **108** (1986) 3130.
- 8 Y. Ayant, N. Kernevez, A. Thévand, L. G. Werbelow, M. Culcasi, G. Gronchi and P. Tordo, *J. Magn. Reson.*, **70** (1986) 446.

- 9 T. Clark, *J. Am. Chem. Soc.*, 107 (1985) 2597.
- 10 D. Feller, E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, 107 (1985) 2596.
- 11 R. L. Petersen, P. J. Nelson and M. C. R. Symons, *J. Chem. Soc., Perkins Trans.*, 2 (1978) 225.
- 12 M. Iwaizumi, T. Kishi, F. Watari and T. Isobe, *Bull. Chem. Soc. Jpn.*, 48 (1975) 3483; M. C. R. Symons and G. D. G. McConnachie, *J. Chem. Soc., Chem. Commun.*, (1982) 851.
- 13 C. J. Rhodes and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, (1989) 1393.