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THE RADICAL ANION OF 2-PHOSPHANAPHTHALENE

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ESR spectra of heteroaromatic phosphorus compounds are of interest because they provide information on the electronic structure of this new class of heterocyclic compounds[1]. Unfortunately, the spectra of the anions of λ^3-phosphorins obtained so far[2] show no ^1H hyper fine structure so that conclusions drawn on this basis are relatively uncertain[3]. We report on the radical anion of 2-phosphanaphthalene[4], which has a highly resolved ESR spectrum, and on some related radical anions.

On reduction with potassium metal of a solution of 2-phosphanaphthalene in THF the brownish colour of the radical anion begins to appear after a few minutes and an ESR spectrum is observed[5] (Fig. 1). The radical anion is stable for several days and does not tend towards fast formation of dimers, as observed in the isoquinoline series[6]. On prolonged exposure to potassium the ESR signal disappears, but there is no indication for the formation of a radical trianion[2].

The ESR spectrum of Fig. 1 could be fully analyzed; the computer simulated spectrum (Fig. 2) is in good agreement with the observed one. The assignment of the coupling constants to the various positions is based on a comparison of the observed data with a HMO calculation and on the following observations:

a. In the radical anions of naphthalene[7], quinoline[6] and isoquinoline[6] the coupling constants at position 3, 6, and 7 are relatively low;

b. the radical anion spectrum of 3-methyl-2-phosphanaphthalene[8] closely resembles that of Fig. 1 which means that the coupling constant at position 3 is low;

c. the radical anion of 1,3-dimethyl-2-phosphonaphthalene[4] gave a poorly resolved ESR spectrum in which the typical separation into two identical halves (caused by phosphorus coupling) is no longer observed, presumably due to the contribution of the additional methylgroup, which implies high spin density at C_1.

Fig. 1

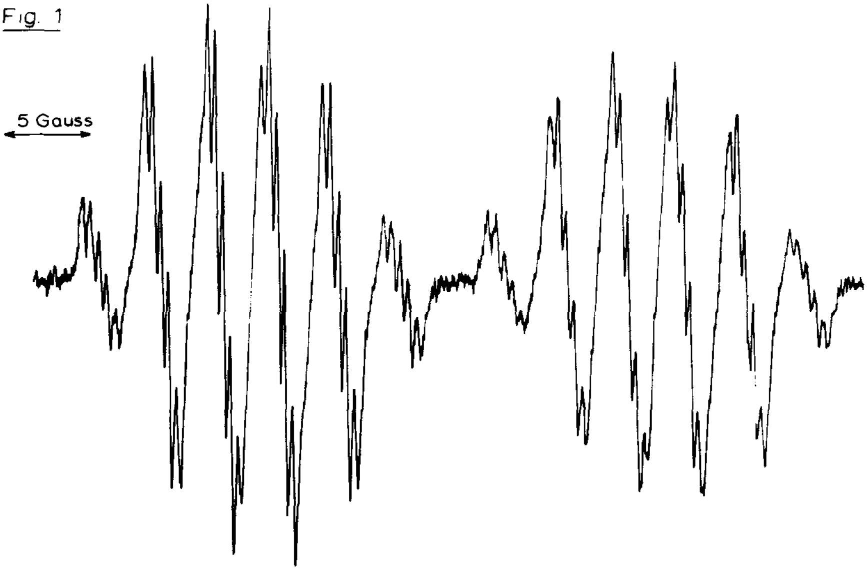
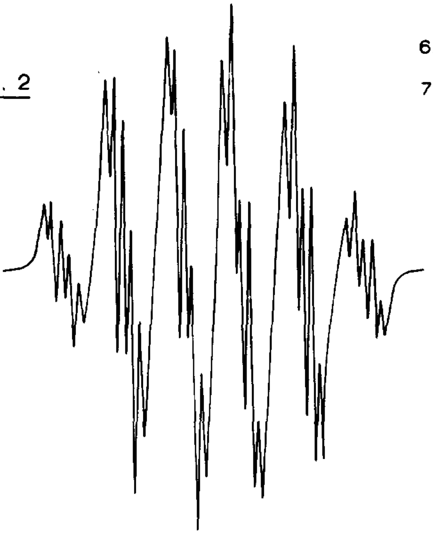


Fig. 2



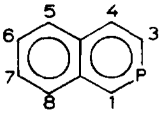
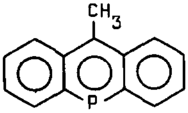


Table 1

position	$a_H^{expt.}$	$a_H^{calc.}$
C_1	7,23	5,65
P	23,6	—
C_3	0,50	0,37
C_4	3,62	3,51
C_5	3,52	3,24
C_6	1,00	2,18
C_7	0,50	0,92
C_8	3,62	4,09

In the HMO calculations we used the parameters $\alpha_P = \alpha_C$, because the electronic behaviour of phosphorus in many respects resembles that of an aromatic CH-group[9,10], and $\beta_{CP} = 0.7\ \beta_{CC}$, as the effective overlap $3p\pi$-$2p\pi$ is expected to be less than $2p\pi$-$2p\pi$[11]. The calculated coupling constants (Table 1) were obtained from the McConnell relation $a_i^H = Q_{CH}^H \cdot \rho_i^\pi$ with $Q_{CH}^H = 25$ G.

From the results of Table 1 the spin density on phosphorus can be calculated to be about 0.2, which leads to a σ-π spin polarization factor $Q^P_{eff.} = 118$ G. In view of $Q^P_{eff.} = 97.9$ for phosphorin cations[3] this value seems to be more reasonable than $Q^P_{eff.} = 31.7$ estimated for phosphorin anions[3].



This value is further corroborated by the ESR spectrum of the radical anion of 10-methyl-9-phosphaanthracene[12], which showed $a^H_{CH_3} = 6.5$ G and $a_P = 33.5$ G, but no further hyperfine structure. HMO calculations using the parameters mentioned above yielded spin densities at positions 9 and 10 of 0.29 and 0.20, respectively. From $a^H_{CH_3} = 1/2\ B^H_{C-CH_3}\rho_C$ (with $1/2\ B^H_{C-CH_3} = 28$ G)[13] we obtain $a^H_{CH_3} = 5.6$ G; similarly, $Q^P_{eff.} = 116$ G is calculated from the spin density on phosphorus in good agreement with the value for 2-phosphanaphthalene.

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