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Radical Anions and Radical Trianions of a Phosphabenzene and Some Diphospha Derivatives of Biphenyl, *p*-Terphenyl and *p,p′*-Quaterphenyl: an ESR and ENDOR Study

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The radical anions and radical trianions of 2,4,6-triphenylphosphabenzene (1), 3,3′,5,5′-tetraphenyl-4λ^3,4′λ^3-diphosphabiphenyl-1,1′ (2), 3,3″,5,5″-tetraphenyl-4λ^3,4″λ^3-diphosphaterphenyl-1,1′:4′,1″ (3) and 3,3‴,5,5‴-tetraphenyl-4λ^3,4‴λ^3-diphosphaquaterphenyl-1,1′:4′,4″:1″,1‴ (4) were studied by ESR and (in part) ENDOR spectroscopy. The singly occupied orbital in the radical anions is symmetric with respect to the vertical mirror plane passing through the phosphorus atom in $1^{\cdot -}$ or two such atoms in $2^{\cdot -}$–$4^{\cdot -}$. Accordingly, the prominent feature of these species is the large and positive ^{31}P coupling constant ($1^{\cdot -}$, + 3.31; $2^{\cdot -}$, + 2.62; $3^{\cdot -}$, + 2.02; and $4^{\cdot -}$, + 1.67 mT), which gives rise to a pronounced hyperfine anisotropy. The anions $1^{\cdot -}$–$4^{\cdot -}$ can thus be regarded as 'P-centred radicals' ($g = 2.0045 \pm 0.0003$). In contrast, the trianions $1^{\cdot 3-}$–$4^{\cdot 3-}$ have to be classified as 'hydrocarbon radicals' ($g = 2.0027 \pm 0.0001$). For $1^{\cdot 3-}$, the hyperfine data could be precisely analysed with the use of the ENDOR technique. As the nodal plane of the singly occupied orbital in this trianion passes through the phosphorus atom, the ^{31}P coupling constant is small and negative (-0.267 mT); the largest value (-0.473 mT) belongs to the two protons in the 3,5-positions of the phosphabenzene ring. The hyperfine patterns of the radical trianions $2^{\cdot 3-}$–$4^{\cdot 3-}$ resemble that of $1^{\cdot 3-}$ with the π-spin population being thus restricted to one phosphabenzene ring and its two phenyl substituents. Such a 'localization' is considered to be due to a degeneracy or near-degeneracy of the singly occupied orbital and to a perturbation caused by the association with three alkali metal counterions. **© 1997 by John Wiley & Sons, Ltd.**

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INTRODUCTION

More than 20 years ago, we described the ESR spectra of the radical anions of phosphabenzene (λ^3-phosphinine) and its 2,4,6-substituted alkyl and phenyl derivatives.[1] Later, another group of workers[2,3a] unsuccessfully attempted to observe the ^{31}P and proton ENDOR spectra of the radical anion of 2,4,6-triphenylphosphabenzene (2,4,6-triphenyl-λ^3-phosphinine; **1**). Prior to these studies,[1,2] it was reported[4] that reduction of **1** with potassium metal in tetrahydrofuran yields not only the radical anion $\mathbf{1}^{\cdot -}$ but also, subsequently, the diamagnetic dianion $\mathbf{1}^{2-}$ and the radical trianion $\mathbf{1}^{\cdot 3-}$. The ESR spectrum of $\mathbf{1}^{\cdot 3-}$ was not analysed. Here, we characterize this triply charged species by its ^{31}P and proton hyperfine data with the use of the ENDOR technique. Further, we present the ESR spectra of the radical anions and the radical trianions of 3,3′,5,5′-tetraphenyl-4λ^3,4′λ^3-diphosphabiphenyl-1,1′ (4λ^3,4′λ^3-diphosphinine; **2**),[5,6] 3,3″,5,5″-tetraphenyl-4λ^3,4″λ^3-diphosphaterphenyl-1,1′:4′,1″ (**3**)[5,6] and 3,3‴,5,5‴-tetraphenyl-4λ^3,4‴λ^3-diphosphaquaterphenyl-1,1′:4′,4″:1″,1‴ (**4**).[6]

EXPERIMENTAL

The syntheses of **1**,[7] **2**,[5] **3**[5] and **4**[6] have been described elsewhere. Reduction of **1**–**4** with potassium metal in 1,2-dimethoxyethane (DME) led, successively, to the radical anions $\mathbf{1}^{\cdot -}$–$\mathbf{4}^{\cdot -}$, the diamagnetic dianions $\mathbf{1}^{2-}$–$\mathbf{4}^{2-}$ and the radical trianions $\mathbf{1}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$. When a solution exhibiting the ESR spectrum of the radical trianion was mixed with that of the neutral compound, the spectrum of the corresponding radical monoanion reappeared, due to comproportionation, e.g. $\mathbf{1}^{\cdot 3-} + \mathbf{1} \rightarrow \mathbf{1}^{\cdot -} + \mathbf{1}^{2-}$ or $\mathbf{1}^{\cdot 3-} + 2 \times \mathbf{1} \rightarrow 3 \times \mathbf{1}^{\cdot -}$. The ESR spectra were recorded on a Bruker ESP-300 spectrometer in the temperature range 203–293 K and

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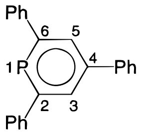

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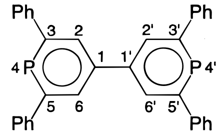

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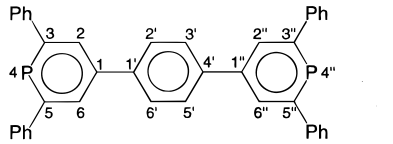

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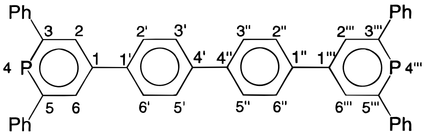

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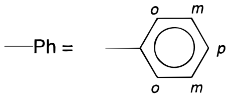

the ENDOR spectra were obtained between 193 and 223 K.

RESULTS

Radical anions

The ESR spectrum of $\mathbf{1}^{\cdot -}$, $g = 2.004\,56 \pm 0.000\,05$, was thoroughly studied in previous work, both in fluid solution[1,2,4] and in a solid matrix.[1] This radical anion exhibits a pronounced g and, in particular, ^{31}P hyperfine anisotropy. The two very broad components, due to the ^{31}P nucleus, are separated by the coupling constant a_P of $+3.31 \pm 0.02$ mT (the signs of the coupling constants here and later are those required by theoretical calculations;[8] solvent DME, counterion K$^+$, temperature 293 K).[1] No hyperfine splittings from the protons could be resolved and renewed attempts to observe the ^{31}P and proton ENDOR spectra were again unsuccessful.

^{31}P hyperfine anisotropy is also a prominent feature in the ESR spectra of $\mathbf{2}^{\cdot -}$, $\mathbf{3}^{\cdot -}$ and $\mathbf{4}^{\cdot -}$, becoming less pronounced when the temperature was raised from 203 to 293 K. These spectra are dominated by the large coupling constant, a_P, of the two equivalent ^{31}P nuclei (Fig. 1). With the expansion of the π-system upon inserting additional phenylene moieties into the molecule, the a_P value decreased from $+2.62$ for $\mathbf{2}^{\cdot -}$ to $+2.02$ for $\mathbf{3}^{\cdot -}$ and to $+1.67$ mT for $\mathbf{4}^{\cdot -}$, whereby the g factor was lowered from 2.004 84 to 2.004 45 and to 2.004 22 in the same sequence (experimental error: ± 0.02 mT in a_P and $\pm 0.000\,05$ in g). Concomittantly, on going from $\mathbf{2}^{\cdot -}$ to $\mathbf{3}^{\cdot -}$ and to $\mathbf{4}^{\cdot -}$, the ^{31}P hyperfine anisotropy tended to average out (Fig.1).

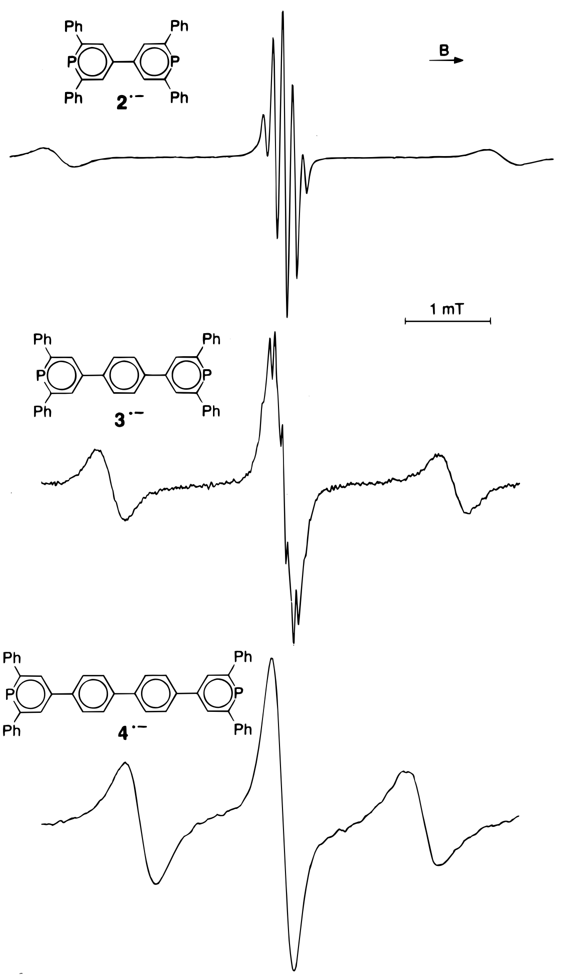

Figure 1. ESR spectra of the radical anions $\mathbf{2}^{\cdot -}$, $\mathbf{3}^{\cdot -}$ and $\mathbf{4}^{\cdot -}$. Solvent DME, counterion K$^+$, temperature 293 K ($\mathbf{2}^{\cdot -}$ and $\mathbf{3}^{\cdot -}$) and 273 K ($\mathbf{4}^{\cdot -}$).

According to calculations by the McLachlan procedure,[8] substantial coupling constants a_{H_μ} for $\mathbf{2}^{\cdot -}$, $\mathbf{3}^{\cdot -}$ and $\mathbf{4}^{\cdot -}$ should be due to the protons attached to the positions μ in the phosphabenzene rings and the intervening phenylene moieties, but not to those in the phenyl substituents (see Discussion). Experimentally, hyperfine splittings from such phosphabenzene and phenylene protons could be observed only for the central ^{31}P component with $M_I(^{31}\text{P}) = 0$, as the outer components with $M_I(^{31}\text{P}) = \pm 1$ were preferentially broadened by anisotropy even at 293 K (Fig. 1). The resolution of these splittings deteriorated on passing from $\mathbf{2}^{\cdot -}$ to $\mathbf{3}^{\cdot -}$ and to $\mathbf{4}^{\cdot -}$, i.e. with increasing number of sets of protons and decreasing absolute values of the coupling constants a_{H_μ}. Whereas the quintet from the four protons at $\mu = 2,6,2'',6''$, with $a_{H_\mu} = -0.118 \pm 0.002$ mT, was fully resolved in the central ^{31}P component of $\mathbf{2}^{\cdot -}$, only a partial resolution of the quintets from the two sets of four protons at $\mu = 2,6,2',6'$ and $2',3',5',6'$, with $a_{H_\mu} = -0.094 \pm 0.003$ and -0.060 ± 0.003 mT, respectively, was achieved for this component of $\mathbf{3}^{\cdot -}$. Overlapping of the expected hyperfine lines from three sets of four phosphabenzene and phenylene protons with still smaller $|a_{H_\mu}|$ values prevented their observation for $\mathbf{4}^{\cdot -}$ (Fig. 1). ENDOR signals could be detected solely for $\mathbf{2}^{\cdot -}$; the separation, 3.31 ± 0.02 MHz, of the observed pair of proton signals agreed with the coupling constant determined from the ESR spectrum.

Radical trianions

The simulation of the ESR spectrum of $\mathbf{1}^{\cdot 3-}$ (Fig. 2) is based on the coupling constants a_P and a_{H_μ} which were associated with the ENDOR signals of a single ^{31}P nucleus and six pairs of protons. The a_P value of -0.267 ± 0.002 mT was derived from one ^{31}P signal at 9.63 MHz and the frequency of the free ^{31}P nucleus (5.89 MHz), while both signals were observed for the six pairs of protons (Fig. 2). Assignments of the six a_{H_μ} values to protons in the individual positions μ are justified by calculations (see Discussion); their relative signs were experimentally verified by general TRIPLE resonance spectroscopy.[3b] The coupling constant a_{H_μ} of -0.473 ± 0.002 mT, with the largest absolute value, was assigned to the two protons at $\mu = 3,5$ in the phosphabenzene ring, while the five remaining a_{H_μ} values were attributed to pairs of protons in the two 2,6-phenyl substituents. These values, -0.249 ± 0.002, -0.188 ± 0.002, -0.075 ± 0.001, $+0.043 \pm 0.001$ and $+0.032 \pm 0.001$ mT, belong to the pairs of protons in the *para*-, *ortho*-, *ortho*-, *meta*- and *meta*-positions, respectively. The occurrence of two different coupling constants, for both the *ortho*- and the *meta*-protons, indicates that the free rotation of the 2,6-phenyl substituents is hindered in $\mathbf{1}^{\cdot 3-}$. Interestingly, the resolution of the ESR spectra varied alternately on going from $\mathbf{1}^{\cdot 3-}$ to $\mathbf{2}^{\cdot 3-}$ to $\mathbf{3}^{\cdot 3-}$ and to $\mathbf{4}^{\cdot 3-}$ (Fig. 3). While $\mathbf{3}^{\cdot 3-}$ exhibited a hyperfine pattern comparable to that of $\mathbf{1}^{\cdot 3-}$, the ESR spectra of the two remaining radical trianions were barely structured ($\mathbf{2}^{\cdot 3-}$) or only partly resolved ($\mathbf{4}^{\cdot 3-}$). In contrast to $\mathbf{1}^{\cdot 3-}$, the ENDOR technique failed for $\mathbf{2}^{\cdot 3-}$, $\mathbf{3}^{\cdot 3-}$ and $\mathbf{4}^{\cdot 3-}$. Nevertheless, the ESR spectra of all four radical trianions $\mathbf{1}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$ had common features which point to a close similarity in their hyperfine data: (i) the detectable hyperfine structure superimposed on the S-shaped ESR absorptions of $\mathbf{2}^{\cdot 3-}$ and $\mathbf{4}^{\cdot 3-}$ matches the resolved patterns of $\mathbf{1}^{\cdot 3-}$ and $\mathbf{3}^{\cdot 3-}$ and (ii) the total width, 2.4 mT, of the ESR spectra is the same for all four radical trianions and so is the g factor, 2.0027, within the limits of ± 0.0001.

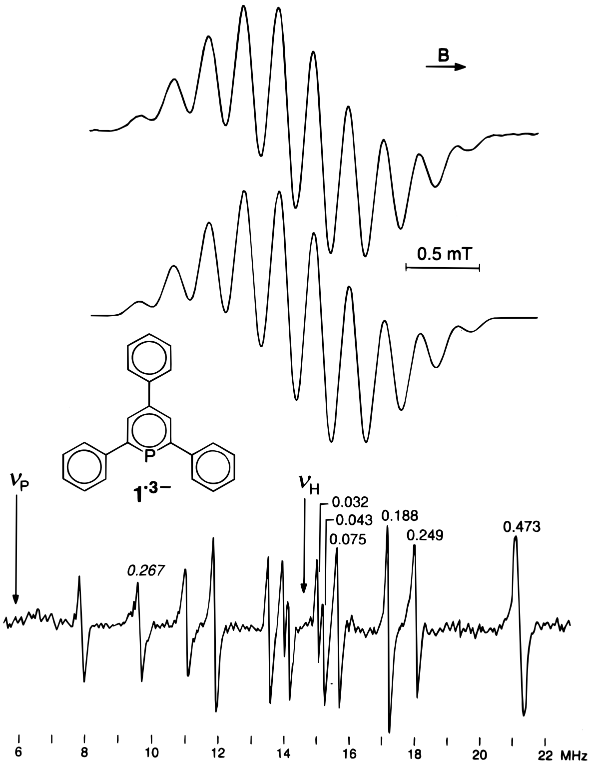

Figure 2. Top: ESR spectrum of the radical trianion $\mathbf{1}^{\cdot 3-}$; solvent DME, counterion K$^+$, temperature 193 K. Middle: simulation of the ESR spectrum with the coupling constants a_P and a_{H_μ} given in the text, Table 1 and below; lineshape Gaussian; linewidth 0.045 mT. Bottom: ^{31}P and proton ENDOR spectrum taken under the same conditions as the ESR spectrum. The numbers above the signals are the absolute values, $|a_P|$ (in italic) and $|a_{H_\mu}|$ in mT, of the coupling constants associated with these signals.

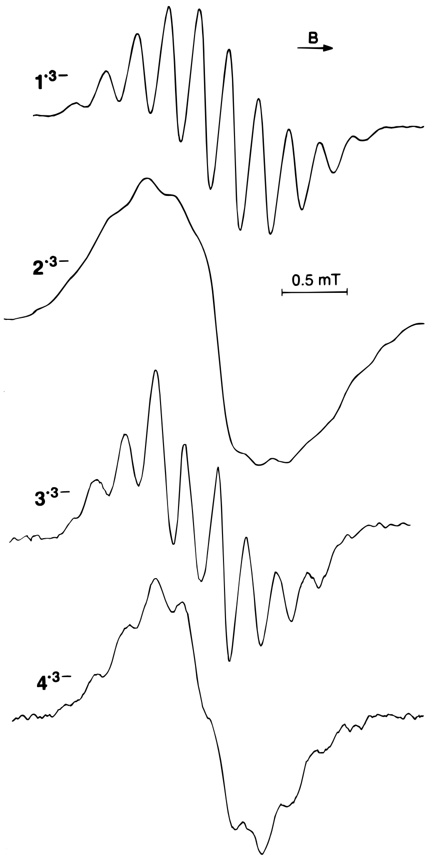

Figure 3. ESR spectra of the radical trianions $\mathbf{1}^{\cdot 3-}$, $\mathbf{2}^{\cdot 3-}$, $\mathbf{3}^{\cdot 3-}$ and $\mathbf{4}^{\cdot 3-}$. Solvent DME, counterion K$^+$, temperature 193 K ($\mathbf{1}^{\cdot 3-}$) and 213 K ($\mathbf{2}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$).

DISCUSSION

Figure 4 shows diagrammatically the LUMOs and the NLUMOs (Next LUMOs) of **1** and **2**, calculated in the frame of the Hückel model (heteroatom parameters $\alpha_P = \alpha + 0.2\beta$ and $\beta_{CP} = 0.75\beta$). The LUMO and NLUMO of **1** correlate with the degenerate antibonding MOs of benzene. The LUMO of **2** corresponds to that of biphenyl, while the NLUMO of **2** represents a 'localized' combination of two accidently degenerate Hückel orbitals and is related to a combination of the likewise accidently degenerate NLUMOs of biphenyl (Fig. 4). Analogously, the LUMOs of **3** and **4** can be connected to those of *p*-terphenyl and *p,p′*-quaterphenyl.

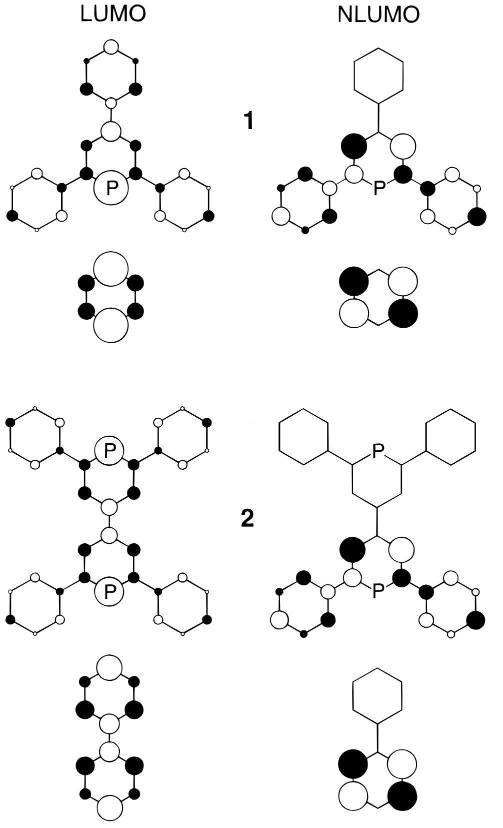

Figure 4. Diagrammatic presentation of the LUMOs and NLUMOs of **1** and **2** as compared with the corresponding MOs of benzene and biphenyl (see text).

As for the NLUMOs of **3** and **4**, they may also be traced back to 'localized' combinations of accidently degenerate Hückel MOs which are antisymmetric with respect to the vertical nodal plane passing through the phosphorus atoms. (The Hückel model of **3** and **4** yields a non-degenerate NLUMO lying slightly below those orbitals which are here referred to as the degenerate NLUMOs. However, this non-degenerate NLUMO is symmetric with respect to the vertical mirror plane passing through the phosphorus atoms and its single occupancy in $\mathbf{3}^{\cdot 3-}$ and $\mathbf{4}^{\cdot 3-}$ would give rise to a very large a_P value, at sharp variance with experimental evidence.) The corresponding orbitals of *p*-terphenyl and *p,p*′-quaterphenyl are accidently fourfold degenerate in the Hückel model, but it is easy to pick out appropriate combinations correlating with the NLUMOs of **3** and **4**, respectively.

In Tables 1 and 2, the π-spin populations ρ_μ at the centres μ, calculated by the McLachlan procedure ($\lambda = 1.0$),[8] are compared with the coupling constants a_P and a_{H_μ} observed for $\mathbf{1}^{\cdot -}$, $\mathbf{1}^{\cdot 3-}$ and $\mathbf{2}^{\cdot -}$–$\mathbf{4}^{\cdot -}$. There is a fair proportionality between the theoretical and experimental values. In particular, the large coupling constants, a_P, of the ^{31}P nuclei in $\mathbf{1}^{\cdot -}$–$\mathbf{4}^{\cdot -}$ correlate well with the π-spin populations ρ_μ at the phosphorus atoms, the proportionality factor being 9.2 ± 0.7 mT. The ρ_μ values are not given for $\mathbf{2}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$ because, in their 'localized' version, they closely match those for $\mathbf{1}^{\cdot 3-}$ at the corresponding centres μ in one phosphabenzene ring and in its two 2,6-phenyl substituents.

Table 1. π-Spin populations, ρ_μ, calculated by the McLachlan procedure and observed ^{31}P and proton coupling constants, a_P and a_{H_μ} (in mT), for $\mathbf{1}^{\cdot -}$ (293 K)and $\mathbf{1}^{\cdot 3-}$ (193 K)

	$\mathbf{1}^{\cdot -}$		$\mathbf{1}^{\cdot 3-}$	
Position μ	ρ_μ	a_P, a_{H_μ}	ρ_μ	a_P, a_{H_μ}
1	+0.389	+3.31 (1P)	−0.013	−0.267 (1P)
3, 5	0.000	–[a]	+0.233	−0.473 (2H)
2, 6-Ph, *o*-	+0.033	–[a]	+0.053	−0.188 (2H); −0.075 (2H)
m-	−0.010	–[a]	−0.011	+0.043 (2H); +0.032 (2H)
p-	+0.039	–[a]	+0.098	−0.249 (2H)
4-Ph, *o*-	+0.049	–[a]	−0.006	–[a]
m-	−0.018	–[a]	−0.001	–[a]
p-	+0.054	–[a]	−0.009	–[a]

[a] Experimental data not available.

Table 2. π-Spin populations, ρ_μ, calculated by the McLachlan procedure and observed ^{31}P and proton coupling constants, a_P and a_{H_μ} (in mT), for $\mathbf{2}^{\cdot -}$–$\mathbf{4}^{\cdot -}$ (293 K)

	$\mathbf{2}^{\cdot -}$			$\mathbf{3}^{\cdot -}$			$\mathbf{4}^{\cdot -}$	
Position μ	ρ_μ	a_P, a_{H_μ}	Position μ	ρ_μ	a_P, a_{H_μ}	Position μ	ρ_μ	a_P, a_{H_μ}
4, 4′	+0.265	+2.62 (2P)	4, 4′	+0.216	+2.02 (2P)	4, 4′	+0.184	+1.67 (2P)
2, 6, 2′, 6′	+0.033	−0.118 (4H)	2, 6, 2″, 6″	+0.025	−0.094 (2H)	2, 6, 2‴, 6‴	+0.021	–[a]
Ph, *o*-	+0.011	–[a]	2′, 3′, 5′, 6′	+0.022	−0.060 (2H)	2′, 6′, 2″, 6″	+0.018	–[a]
m-	−0.005	–[a]	Ph, *o*-	+0.009	–[a]	3′, 5′, 3″, 5″	+0.017	–[a]
p-	+0.013	–[a]	*m*-	−0.003	–[a]	Ph, *o*-	+0.007	–[a]
			p-	+0.011	–[a]	*m*-	−0.003	–[a]
						p-	+0.010	–[a]

[a] Experimental data not available.

Moreover, the exact hyperfine data a_P and a_{H_μ} for $\mathbf{2}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$, which should also be similar to those for $\mathbf{1}^{\cdot 3-}$, are experimentally not available.

For $\mathbf{1}^{\cdot -}$ and $\mathbf{4}^{\cdot -}$, the large width of the ESR lines and the reluctance to yield the ENDOR spectrum are ascribed to the high π-spin populations at the phosphorus atoms which results in the pronounced ^{31}P hyperfine anisotropy, as stated previously in the case of $\mathbf{1}^{\cdot -}$.[1,2,3a] On the other hand, for $\mathbf{2}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$, the broadening of the ESR lines and the failure to observe the ENDOR spectrum ought to be caused by the degeneracy or near-degeneracy of the singly occupied orbitals which impedes the saturation of an ESR line[9] [such orbitals of appropriate symmetry (see earlier note) are accidently degenerate in the Hückel model].

Association of the radical trianions $\mathbf{2}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$ with their three alkali metal counterions ('ion pairing') is considered to be responsible for the localization of the π-spin population in one half of the molecule. It can also be the reason for the steric hindrance to rotation of the phenyl substituents, which was observed for $\mathbf{1}^{\cdot 3-}$ and, presumably, also occurs in $\mathbf{2}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$. From the temperature range (193–223 K) in which the ENDOR spectrum of $\mathbf{1}^{\cdot 3-}$ was obtained, and from the separations of the signals due to the two non-equivalent *ortho*-protons (1.58 MHz) and of the two likewise non-equivalent *meta*-protons (0.15 MHz), it can be estimated that the activation barrier to rotation is higher than 30 kJ mol^{-1}.[10]

CONCLUSIONS

In the radical anions $\mathbf{1}^{\cdot -}$–$\mathbf{4}^{\cdot -}$, the singly occupied orbitals are symmetric with respect to the vertical mirror plane passing through the phosphorus atoms which bear a substantial part of the total π-spin population (Tables 1 and 2). Accordingly, the ^{31}P coupling constants are large and positive (+1.7 to +3.4 mT) and their anisotropy is the prominent feature of these anions, which may be regarded as 'P-centred radicals.' The enhanced *g* factors, 2.0042–2.0048, are also consistent with such a classification. In contrast, the singly occupied orbitals of the radical trianions $\mathbf{1}^{\cdot 3-}$–$\mathbf{4}^{\cdot 3-}$ have a vertical nodal plane through the phosphorus atoms and the ^{31}P coupling constants are relatively small and negative (−0.267 mT for $\mathbf{1}^{\cdot 3-}$). These trianions can thus be classified as 'hydrocarbon radicals,' in line with their *g* factor of 2.0027 ± 0.0001, characteristic of π-radical anions without heteroatoms.[11]

Acknowledgement

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