Spin Densities in the Radical Anion of 3,3′-Bipyridine

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Synopsis. The ESR spectrum of the radical anion of 3,3′-bipyridine has been measured. The hfs constants agree with the calculated values based on the spin densities using the McLachlan method.

Although the ESR spectra of the radical anion of 2,2′-[1-4] and 4,4′-bipyridines[5-7] are known, the radical anion of 3,3′-bipyridine has not been investigated by ESR tecniques. Therefore, it is of interest to measure the ESR spectrum of the radical anion of 3,3′-bipyridine in order to compare the spin distribution of this radical anion with those of 2,2′- and 4,4′-bipyridine. We wish to report here an ESR study of the radical anion of 3,3′-bipyridine.

The radical anion was generated by the reduction of 3,3′-bipyridine, which had been prepared from 3,3′-bipyridine-2,2′-dicarboxylic acids by the method of Smith,[8] with potassium metal in 1,2-dimethoxyethane (DME). This solution was investigated by ESR spectroscopy in the temperature range from 85 to −85 °C.

The intense well-resolved ESR spectrum measured at 80 °C of the radical anion of 3,3′-bipyridine is shown in Fig. 1a (g=2.0024). Figure 1a consists of hyperfine splitting (hfs) constants due to the equivalent protons, a_H=0.626, 0.582, and 0.115 mT and the nitrogens, a_N=0.094 mT (see Table 1). Using these parameters, the computer-simulated spectrum shown in Fig. 1b was obtained; it agreed well with the observed spectrum. On the other hand, we could not obtain the well-resolved ESR spectra at temperature lower than room temperature. Probably, this is due to the overlap of the hfs constants, because these spectra have a slight different values from the above hfs constants. In consequence, we can not yet analyze these spectra.

In order to assign the hfs constants, we have carried out MO calculations.[9] The results are summarised, together with the observed hfs constants, in Table 1. The most interesting features are the approximately equal and large hfs constants of the γ- and ε-protons, and the hfs constant of the α-protons, which is smaller than the simulated linewidth, 0.007 mT.

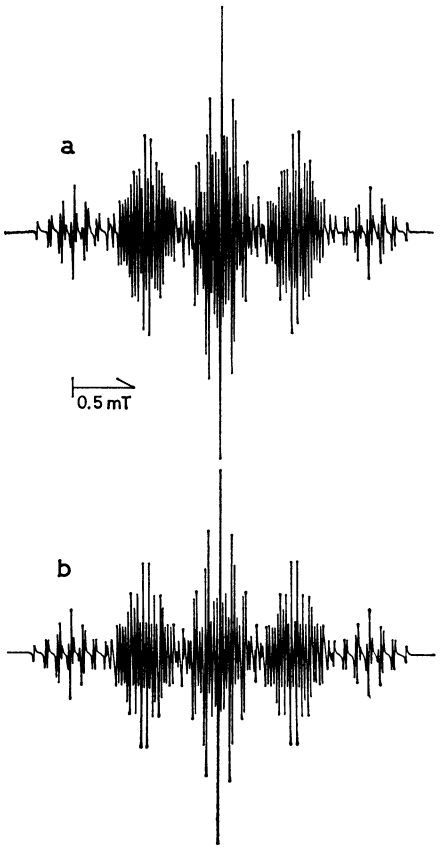

Fig. 1. (a) The observed ESR spectrum of the radical anion of 3,3′-bipyridine: solvent, DME; counterion, K^+; at 80 °C. (b) The spectrum simulated by means of the hfs constants listed in Table 1: lineshape, Lorentzian; linewidth, 0.007 mT.

Table 1. The hfs constants of the radical anion of 3,3′-bipyridine and its calculated spin densities

Position	Calculated spin density		Calculated hfs const[c]	Observed hfs const[d]
	HMO[a]	McLachlan[b]	mT	mT
α	0.012	−0.006	0.016	...
β(N)	0.055	0.038	0.093	0.094
γ	0.181	0.226	0.632	0.626
δ	0.002	−0.040	0.112	0.115
ε	0.157	0.193	0.540	0.582
ζ	0.093	0.089	...	—

a) Parameters, h_N=0.7 and k_{CN}=k_{CC}=1.0. b) Parameter, λ=0.8. c) Obtained by the use of this equation; a_x=$Q_x\rho$, with Q_N=|2.45| and Q_H=|2.8| mT, and using the calculated McLachlan-spin densities. d) Potassium-counterion in DME at 80 °C.

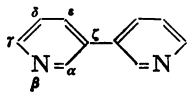

Table 2. The hfs constants of the radical anions of biphenyl, bipyridines, and bipyrimidine

Radical anion	hfs constants/mT				
	$a_{H\alpha}$	$a_{H\beta}$	$a_{H\gamma}$	$a_{H\delta}$	$a_{H\varepsilon}$
Biphenyl[a]	0.266	0.041	0.531	0.041	0.266
4,4′-Bipyridine[b]	0.235	0.043	0.364[e]	0.043	0.235
2,2′-Bipyridine[c]	0.258[e]	0.057	0.470	0.120	0.106
2,2′-Bipyrimidine[d]	0.141[e]	0.015	0.498	0.015	0.141[e]

a), b), c), and d) Values reported in Refs. 10, 6, 4, and 11. e) These are the hfs constants of the nitrogen atoms.

We can recognize the suitability of the assignments for the hfs constants (see Table 1) of the radical anion of 3,3′-bipyridine, which are compared with the hfs constants of various radical anions of biphenyl,[10] 2,2′- and 4,4′-bipyridines,[4,6] and 2,2′-bipyrimidine[11] in Table 2. That is, the hfs constant of the nitrogens for the radical anion of 3,3′-bipyridine is a usual value, while the $a_{H_\alpha} \simeq 0$ and $a_{H_\beta} = 0.582$ mT values are unsual in comparison with the hfs constants of other bipyridines. However, the hfs constants agree well with the MO calculated values, as is shown in Table 1. Therefore, as an example to facilitate comparison with the a_{H_α} and $a_{H_\beta} = 0.235$ mT of the radical anion of biaxial symmetric 4,4′-bipyridine,[6] the computed average value of the hfs constant for the radical anion of 3,3′-bipyridine is about 0.29 mT and is normal. All thing considered, each of the three radical anions of bipyridine isomers has a proper hfs constant and a different MO calculated spin-density distribution[3,6] because each molecule containing two nitrogen atoms has a different space-coordination.[12,13] In conclusion, we have found that the ESR spectrum of the radical anion of 3,3′-bipyridine consists of the hfs constants shown in Table 1, and the spin densities calculated using the McLachlan method[9] satisfy the experimental values.

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