An Electron Spin Resonance Study of 2-Pyridyl in γ-Irradiated Pyridine

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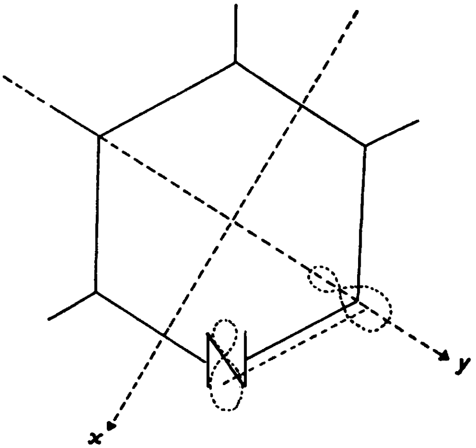
EXPOSURE of solid perdeuteropyridine to γ-radiation yields a radical, thought to be the perdeuteropyridine cation, having an e.s.r. spectrum consisting of an almost isotropic triplet with a hyperfine coupling of 30 gauss.[1,2] This implies that the unpaired electron is in an orbital which has about 0·06 2*s*-character on nitrogen, but negligible 2*p*-character, and yet, if the identification were correct, the electron should be almost entirely confined to an orbital which should bear considerable resemblance to the σ-lone-pair orbital of pyridine. Furthermore, as with the isoelectronic phenyl radical, there should be a strong hyperfine interaction with the two *ortho*-protons and a smaller coupling to the *meta*-protons. The extra lines detected when pyridine is irradiated cannot be assigned in this way.

It is possible that the pyridine cation is a π-radical rather than having the *ortho*-structure assumed here. However, the relatively large 2*s*-population and small 2*p*-population deduced from the ^{14}N hyperfine coupling constants are even less reconcilable with this formulation.

The purpose here is to suggest that the radical is not the pyridine cation, but its conjugate base, 2-pyridyl (I).

At high gain, pairs of satellite lines have been detected, which have been analysed in terms of ^{13}C hyperfine interaction to give the parameters given in the Table. We also give the corresponding molecular parameters (c_s^2 and c_p^2) derived in the usual manner.[3]



(I)

FIGURE

Diagram of 2-pyridyl radical showing proposed principal axes of g*-tensor. (The* y *axis is perpendicular to the plane.)*

TABLE

g-Values and hyperfine parameters of the radical in γ-irriadiated perdeuteropyridine

	A$_{\text{iso}}$	2B	c^2_s	c^2_p	λ^2	g_x	g_y	g_z
^{13}C	170	30	0·15	0·45	3·0	2·001	2·002	2·000
^{14}N	29·7	5·5	0·06	0·16	2·7			

An analysis of the *Q*-band spectrum of irradiated perdeuteropyridine has given the principal *g*-values and ^{14}N hyperfine coupling constants listed in the Table. These have also been tentatively analysed to give ^{14}N atomic parameters on the assumption that the measured values relate to the principal directions of the *g*-tensor, which we expect to lie relatively close to the axes given in the Figure. The very small anisotropy found in the *X*-band spectrum can then be understood as stemming fortuitously from the lack of common directions for the ^{14}N hyperfine and *g*-tensors, and the fact that spin density will reach the nitrogen atom both by in-plane π-bonding as indicated in (I) and also by delocalisation into the C–N σ-bond.[3]

Further details, together with the results of parallel studies of various substituted pyridines, pyridinium salts, and pyridine in certain glasses will be given elsewhere. Here we draw attention to the link between this radical and the intermediate, benzyne, which has one less electron in the in-plane pseudo-π-system. The fact that the spin-density in radical (I) is largely on carbon rather than nitrogen is to be expected for a three-electron system, and follows closely the results obtzined for nitrogen in diamond.[4] Also, the *p*/*s* ratio (λ^2) which is considerably greater than two on carbon and to a lesser extent on nitrogen corresponds to slight increases in the <C–C–N and <C–N–C bond angles.[4]

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