

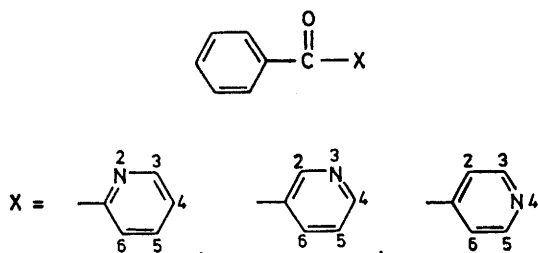
## An Electron Spin Resonance Investigation of the Radical Anions of the Benzoylpyridines

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The radical anions of the three benzoylpyridines have been prepared by electrochemical reduction in dimethylformamide. The interpretation of their e.s.r. spectra reveals that the phenyl ring rotates freely in each radical anion. However the rotation of the pyridine ring is restricted in the radical anion of 4-benzoylpyridine. It is possible that the rotation of the pyridine ring is also restricted in the radical anion of 2-benzoylpyridine but in the radical anion of 3-benzoylpyridine the pyridine ring appears to be rotating at an intermediate rate. Molecular orbital calculations have been employed as an aid to the assignment of the splitting constants in each of the radical anions.

RADICAL anions of aromatic carbonyl compounds may be readily generated in suitable solvents by alkali metal or electrochemical reduction.<sup>1-5</sup> When generated by alkali-metal reduction the alkali-metal cation forms an ion pair with the radical anion in which the cation tends to be located near the electronegative carbonyl oxygen. Consequently, if the molecule contains two equivalent carbonyl groups the cation can migrate from one carbonyl group to the other leading to some interesting linewidth effects in the e.s.r. spectrum.<sup>6,7</sup>

In our previous investigations of aromatic carbonyl compounds the radical anions were generated electrochemically and consequently cation migration processes were not observed.<sup>1,2</sup> However interesting linewidth effects are sometimes observed when rotational conformers are present. Two such conformers were observed in the electrochemically generated radical anion of 3-acetylpyridine.<sup>8</sup> However no linewidth effects were reported in the e.s.r. spectrum of this radical anion which, presumably, implies that the rate of interconversion between the two conformers is slow. However our interest in rotational conformers of radical anions derived from aromatic carbonyl compounds has led us to reinvestigate the e.s.r. spectra of the three benzoylpyridines.<sup>9,10</sup> In this paper we report the results obtained from an examination of well resolved e.s.r. spectra of these radical anions.



### RESULTS AND DISCUSSION

**4-Benzoylpyridine.**—4-Benzoylpyridine is readily reduced electrochemically in dimethylformamide to yield a blue solution of the radical anion with a characteristic e.s.r. spectrum [see Figure 1(a)]. Spectra were recorded over the temperature range 233–293 K and showed

little variation. In principle the e.s.r. spectrum of this radical anion should be the simplest of the three benzoylpyridines to interpret. If rotational conformers are not present an interpretation based on four 1 : 2 : 1 triplets, a 1 : 1 doublet, and a 1 : 1 : 1 triplet would be expected. However, although 1 : 2 : 1 triplets are observable in the spectrum, it is apparent that at least one of the anticipated 1 : 2 : 1 triplets is present as a pair of doublets. A full computer simulation of the spectrum was therefore obtained [Figure 1(b)]. The successful simulation includes three 1 : 1 doublets ( $a_H$  187, 277, and 311  $\mu$ T). In order to discover which of these doublets should be assigned to the phenyl ring the radical anion of 4-(4-t-butylbenzoyl)pyridine was prepared. The e.s.r. spectrum of this radical anion, although having a smaller overall width, was similar in its main features to that of the parent ketone. A computer simulation was again obtained for this radical anion and again reveals that one of the expected 1 : 2 : 1 triplets appears as a pair of doublets ( $a_H$  285 and 345  $\mu$ T). It is therefore apparent that the doublet with  $a_H$  187  $\mu$ T is to be assigned to the *para*-position in the phenyl ring. On this basis, therefore, it is now possible to assign the triplets with  $a_H$  58 and 152  $\mu$ T to the phenyl ring. This assignment is based upon a comparison of the relative values of the splitting constants in benzophenone<sup>4</sup> with those in the parent ketone. Consequently two large 1 : 1 doublets ( $a_H$  277 and 331  $\mu$ T) and a 1 : 1 : 1 triplet ( $a_N$  350  $\mu$ T) together with the remaining small 1 : 2 : 1 triplet ( $a_H$  19  $\mu$ T) can be assigned to the pyridine ring (see Table 2).

The lack of symmetry in the pyridine ring contrasts with the symmetry of the phenyl ring. It is not clear from the computer simulation whether the non-equivalence in the pyridine ring is complete. It is possible that the small 1 : 2 : 1 triplet may, in fact, result from two nearly equivalent protons within the resolution of the spectrum. Indeed, in view of the non-equivalence of the protons at the 2 and 6 positions (an assignment based upon the molecular orbital calculations discussed later) some non-equivalence at the 3 and 5 positions would be expected. (This observation is in accord with that for the radical anion of 4-acetylpyridine, where the splitting constants associated with both the two *ortho*- and two *meta*-protons are non-equivalent).<sup>4</sup> The equivalence of

the *ortho*- and *meta*-protons in the phenyl ring indicates that the rotation of this ring is not restricted. (If the rotation were restricted the *ortho*- and *meta*-protons *trans* to the carbonyl group would have different splitting constants to those *cis* to the carbonyl group). It is

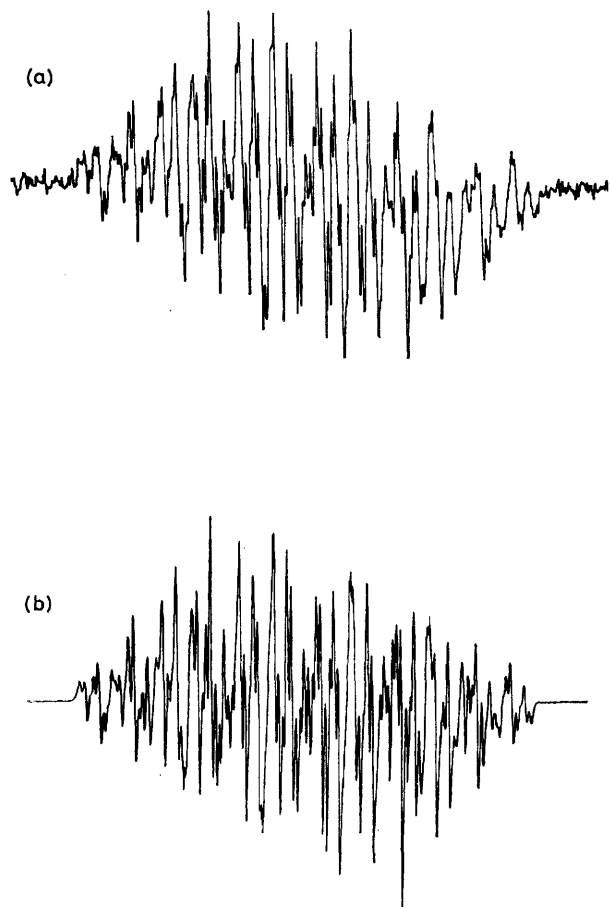


FIGURE 1 (a) The e.s.r. spectrum of the 4-benzoylpyridine radical anion in dimethylformamide at 233 K and (b) a computer reconstruction based on the splitting constants given in Table 2

apparent therefore that while the phenyl ring in the radical anion of 4-benzoylpyridine appears to rotate freely, the pyridine ring does not.

This conclusion is interesting. One possible explanation could be that the barrier to ring rotation increases significantly in the unsymmetric ketone. However a second factor which could be quite important is the magnitude of the unpaired electron density on the 2 and 6 positions in the pyridine ring compared with that on the corresponding positions in the phenyl ring. The unpaired electron density is almost twice as great in the former case and consequently the increased interaction with the electronegative carbonyl oxygen atom would have significant influence on the barrier to rotation.

**2-Benzoylpyridine.**—2-Benzoylpyridine is readily reduced electrochemically in dimethylformamide to yield a blue solution of the radical anion with a characteristic e.s.r. spectrum [see Figure 2(a)]. Spectra were again

recorded over a temperature range and, apart from changes in resolution, showed no significant variation. Interpretation of the e.s.r. spectrum of this radical anion was slightly more complicated due to the large number of 1 : 1 doublets present. However it is apparent from an examination of the spectrum that two 1 : 2 : 1 triplets are present and this observation was confirmed by a computer simulation [see Figure 2(b)] based on the splitting constants summarised in Table 2. In order to identify the doublet associated with the *para* position in the phenyl ring the e.s.r. spectrum of the 2-(4-*t*-butylbenzoyl)pyridine radical anion was also recorded. Again this spectrum has a reduced overall width compared with that of the parent ketone and, from a computer simulation of the spectrum (see Table 2), it is apparent that the doublet splitting of 272  $\mu\text{T}$  is to be assigned to the *para*-proton.

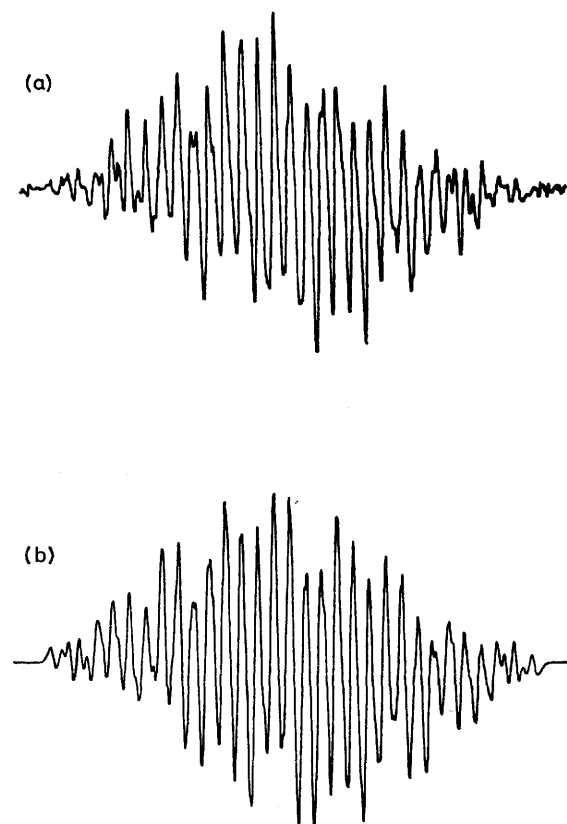


FIGURE 2 (a) The e.s.r. spectrum of the 2-benzoylpyridine radical anion in dimethylformamide at 253 K and (b) a computer reconstruction based on the splitting constants given in Table 2

The assignment of the proton splitting constants to the various positions in the pyridine ring is not readily undertaken without the aid of molecular orbital calculations. The largest of the remaining large doublet splittings ( $a_{\text{H}} 490 \mu\text{T}$ ), however, can be provisionally assigned to the proton at the 4-position of the pyridine ring. It is not possible from this interpretation to comment at this stage on the rotation of the pyridine ring. Again the molecular orbital calculations, to be discussed

later, allow some observations to be made. However, it is clear from the equivalence of the two *ortho*- and two *para*-protons in the phenyl ring that the phenyl ring is freely rotating in the radical anion of this benzoylpyridine.

**3-Benzoylpyridine.**—The electrochemical reduction of 3-benzoylpyridine in dimethylformamide again produces a blue solution of the radical anion with a characteristic e.s.r. spectrum [see Figure 3(a)]. Spectra were recorded over a temperature range but unlike the spectra of the other radical anions these spectra were temperature dependent. In particular the hyperfine structure in the central region of the spectrum varied markedly with temperature. In addition, at higher temperatures the spectrum broadened to such an extent that little useful information could be obtained. However at lower temperatures narrow line spectra were obtained and a computer reconstruction of these has been attempted. Again two 1 : 2 : 1 triplets ( $a_H$  78 and 220  $\mu T$ ) are readily observable and have been assigned, respectively, to the *ortho*- and *meta*-protons of the phenyl ring. Following the information obtained on the relative magnitude of the splitting constants within the phenyl ring in the radical anions of the two benzoylpyridines previously discussed, a doublet splitting of *ca.* 230–300  $\mu T$  is expected from the *para*-proton and is

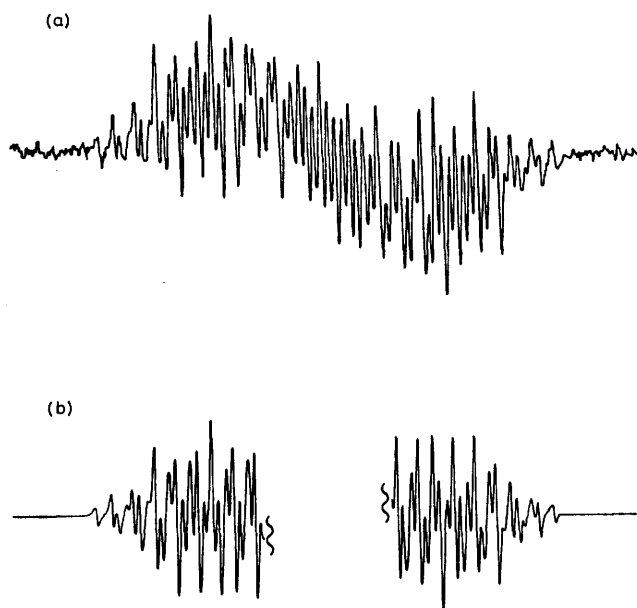


FIGURE 3 (a) The e.s.r. spectrum of the 3-benzoylpyridine radical anion in dimethylformamide at 268 K and (b) a computer reconstruction of the wings of the spectrum based on the splitting constants given in Table 2

indeed observed (290  $\mu T$ ). A satisfactory simulation of the wings of the spectrum also requires two other small splitting constants, a 1 : 1 doublet (104  $\mu T$ ) and a 1 : 1 : 1 triplet ( $a_N$  115  $\mu T$ ). We also believe that the simulation requires a further doublet splitting of 490  $\mu T$  but have found some difficulty in proceeding to a complete simulation of this spectrum.

The temperature effects observed in this spectrum suggest a source of this difficulty. The equivalence of the *ortho*- and *meta*-protons in the phenyl ring again indicate that this ring is rotating freely. However we believe that the pyridine ring is not locked as in 4-benzoylpyridine, but may be rotating at an intermediate rate. Clearly the splitting constants associated with each position in the pyridine ring will differ in the two conformers. Indeed in the radical anion of 3-acetylpyridine the splitting constants associated with the pyridine ring in both conformers have been determined (see Table 1).<sup>8</sup> It can be seen that while the splitting constants associated with the 3-, 4-, and 5-positions in each conformer are similar, those at the 2- and 6-positions differ significantly. The consequence of an intermediate rate of rotation can now be predicted. The positions of many of the lines in the spectrum move only slightly upon a change of conformation and, therefore, remain relatively sharp. However the positions of the lines arising from the 2- and 6-positions change dramatically and will broaden considerably at certain conformer lifetimes. Consequently while a computer reconstruction based upon a constant linewidth might be reasonably successful, particularly in the wings of the spectrum, it cannot achieve a complete simulation when linewidth effects are present. Therefore, at intermediate lifetimes it is possible to determine the sum  $a_2 + a_6$  from the spectrum (= 655  $\mu T$ ) but not the individual values of  $a_2$  and  $a_6$ . A computer reconstruction of the wings of the spectrum based upon the splitting constants that have been determined is shown in Figure 3(b) (see also Table 2).

TABLE 1

Hyperfine splitting constants (in  $\mu T$ ) for both conformers of the 3-acetylpyridine radical anion (taken from ref. 8)

	Position				
	2	3	4	5	6
<i>cis</i> -Conformer	260	115	789	130	573
<i>trans</i> -Conformer	480	146	773	108	338

**Molecular Orbital Calculations.**—Molecular orbital calculations, together with the McLachlan modification,<sup>11</sup> were used to aid the assignment of the splitting constants in each of the benzoylpyridines. A large number of variable parameters are required in these calculations. Two parameters,  $k_{OX}$  and  $h_X$  [see equations (1) and (2)] are required for each of the heteroatoms, and a further variable parameter ( $k_{CO}$ ) is required to allow for the non-planarity of the rings with respect to the carbonyl groups. Each of these parameters were varied in turn to establish its optimum value with the constraint that the same parameter was applied to each of the benzoylpyridines.

$$\beta_{OX} = k_{OX}\beta_{CO} \quad (1)$$

$$\alpha_X = \alpha_O + h_X\beta_{CO} \quad (2)$$

Reasonable values of  $k_{CO}$  and  $h_O$  have been established. In particular the values which have proved successful for

benzophenone should also be appropriate for the benzoylpyridines.<sup>4,8</sup> The optimum values of these parameters has been established as  $k_{CO} = 1.6$  and  $h_o = 1.5$ . Nevertheless, when the value of  $h_o$  was varied in the benzoylpyridines from 1.3 to 1.7, the unpaired electron densities were found to be relatively insensitive to this parameter. In contrast, the value of  $k_{CN}$  has a pronounced effect on the unpaired electron densities in the pyridine ring. Acceptable values were found within the range 0.9—1.1 with a best value of 1.1. The value of  $h_N$  was varied from 0.25 to 1.25 with the best value differing slightly from ketone to ketone. However the best value for all three benzoylpyridines appears to be *ca.* 0.5. The two  $k_{CC}$  parameters remain. The variation of these parameters allows the total unpaired electron density in each ring to be varied. The splitting constants are readily assigned to the phenyl ring protons; the values for the 2- and 3-benzoylpyridines are very similar and a value of  $k_{CC} = 0.9$  seems appropriate. However the unpaired electron densities are significantly

the experimental (e.s.r.) unpaired electron densities is found if the parameter is applied to the 6-position (*i.e.* with the carbonyl oxygen and pyridine nitrogen in a *trans*-configuration as indeed might be anticipated). If, however, our observation that the pyridine ring is rotating at an intermediate rate in 3-benzoylpyridine is correct, then the preferred conformer cannot be established for this radical anion. We have nevertheless performed calculations with an auxiliary inductive parameter introduced at both the 2- and 6-positions in this ketone in order to predict the variation of the unpaired electron density and hence of the splitting constants in the two conformers. The results of these two sets of calculations are in good agreement with those for 3-acetylpyridine where the spectrum of both conformers has been obtained.<sup>8</sup> Little difference in the unpaired electron density at the 3-, 4-, and 5-positions is predicted, but the unpaired electron density changes dramatically at the 2- and 6-positions (see Table 2).

The remaining parameter,  $\lambda$ , in the McLachlan modifi-

TABLE 2

A summary of the experimental and theoretical hyperfine splitting constants (in  $\mu\text{T}$ ) for the three benzoylpyridine radical anions

	Position							
	<i>o</i>	<i>m</i>	<i>p</i>	2	3	4	5	6
2-Benzoylpyridine (experimental)	221	78	272	287	46	490	0	155
2-(4-t-Butylbenzoyl)pyridine (experimental)	221	75	—	294	51	500	0	157
2-Benzoylpyridine (theoretical <i>cis</i> -conformer)	224	(-) 75	289	293	(-) 104	376	(-) 59	244
2-Benzoylpyridine (theoretical <i>trans</i> -conformer)	219	(-) 73	282	338	(-) 109	363	0	182
3-Benzoylpyridine (experimental)	220	78	290	*	115	490	104	*
3-Benzoylpyridine (theoretical <i>cis</i> -conformer)	228	(-) 75	304	194	(-) 99	416	(-) 117	361
3-Benzoylpyridine (theoretical <i>trans</i> -conformer)	232	(-) 76	311	277	(-) 138	393	(-) 76	270
4-Benzoylpyridine (experimental)	152	58	187	277	19	350	19	331
4-(4-t-Butylbenzoyl)pyridine (experimental)	143	63	—	285	15	365	15	345
4-Benzoylpyridine (theoretical)	156	(-) 52	206	255	0	417	(-) 64	322

\*  $a_2 + a_6 = 655 \mu\text{T}$ .

lower in the phenyl ring of 4-benzoylpyridine where a value of 0.75 for this parameter appears appropriate. The total unpaired electron density in the pyridine ring requires a higher value of  $k_{CC}$  than for the phenyl ring. The value appropriate to the results summarised in Table 2 is 1.0.

Although the *ortho*- and *meta*-protons are equivalent in the radical anion of each ketone the protons in the pyridine ring of 4-benzoylpyridine are non-equivalent. This non-equivalence, due to restricted rotation of the pyridine ring, can be allowed for by the introduction of an auxiliary inductive parameter ( $\delta = 0.15$ ) on the carbon atom at the 2- (or 6-) position [see equation (3)].<sup>4,8</sup> The introduction of this parameter into the calculation for 4-benzoylpyridine raises a major problem for the two

$$\alpha_C = \alpha_C + \delta\beta_{CC} \quad (3)$$

remaining benzoylpyridines. If the pyridine ring is 'locked' in these two ketones then the auxiliary inductive parameter should be applied to either the 2- or the 6-position depending upon the preferred conformer. In the case of 2-benzoylpyridine the preferred fit with

ation was varied from 0.5 to 1.25 in each calculation. The optimum value would appear to be *ca.* 1.20 and this value has been used to obtain the values quoted in Table 2. The theoretical splitting constants have been obtained using equations (4) and (5) (where  $\rho_a$  and  $\rho_b$  are the unpaired electron densities on the carbon atoms immediately adjacent to the nitrogen atom, and  $Q_{CH^H} = |2.50|$ ,  $Q_{N^N} = 2.75$ , and  $Q_{CN^N} = -0.15 \text{ mT}^{12}$ ).

$$a_H = Q_{CH^H}\rho \quad (4)$$

$$\alpha_N = Q_{N^N}\rho_N + Q_{CN^N}(\rho_a + \rho_b) \quad (5)$$

#### EXPERIMENTAL

*Materials.*—Tetra-n-butylammonium iodide and dimethylformamide were obtained commercially; the latter was dried over a molecular sieve before use. The benzoylpyridines, also obtained commercially (Aldrich), were recrystallised from light petroleum (b.p. 100—120 °C) before use. Samples of the (4-t-butylbenzoyl)pyridines were prepared from *p*-t-butylbromobenzene<sup>13,14</sup> employing a Grignard reaction with the appropriate cyanopyridine (Aldrich) in ethereal solution. The mixture was refluxed for 7 h an

then acidified with hydrochloric acid. The resulting aqueous layer was further refluxed for 3 h, neutralised with aqueous sodium hydroxide, and the resulting product extracted with ether. The ethereal solution of the product was then washed and dried over  $\text{CaCl}_2$  to yield the corresponding (4-t-butylbenzoyl)pyridine.

*Procedure.*—Dimethylformamide solutions for electrolytic reduction were in the range  $1\text{--}5 \times 10^{-3}\text{M}$  with 0.1M-tetra-n-butylammonium iodide as supporting electrolyte. Solutions of the radical anions were prepared for e.s.r. study as described.<sup>2</sup>

*Spectroscopic Measurements.*—E.s.r. spectra were recorded on a Varian E3 spectrometer employing a Varian E4557 variable temperature unit. Spectra simulations were carried out employing a Data General Nova 1220 computer.

*Calculations.*—Molecular orbital calculations were performed with the aid of an ICL 2960 computer.

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