

## Muon Spin Rotation Studies of *cis* $\rightleftharpoons$ *trans* Isomerisation in 1-(2-Pyridyl)ethyl Radicals

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The activation energy for *cis*  $\rightleftharpoons$  *trans* isomerisation of the 1-(2-pyridyl)ethyl radical has been measured by the muon spin rotation technique.

Radical stabilisation is of considerable current interest. Arnold and Dust<sup>1</sup> have suggested that the stabilising effect of substituents in benzyl radicals may be quantified in terms of a parameter  $\sigma^*$ , derived from the  $\alpha$ -methylene proton coupling constants by an equation of the form (i); where  $x$  is the coupling for the substituted benzyl radical and  $x_0$  that for the unsubstituted radical.

$$\sigma^* = 1 - (x/x_0) \quad (i)$$

The solution-phase e.s.r. spectra of the three isomeric pyridylmethyl radicals have recently been measured<sup>2</sup> by 'correlation methods': in each case, the methylene proton coupling constant is greater than that in benzyl itself, and so, negative  $\sigma^*$  values are obtained from equation (i) (*i.e.* the pyridyl substituents are less stabilising than is phenyl, the order being 4-pyridyl < 2-pyridyl < 3-pyridyl < phenyl). We

find a similar order of  $\beta$ -muon couplings in the muonated aryl-substituted ethyl radicals (Table 1).

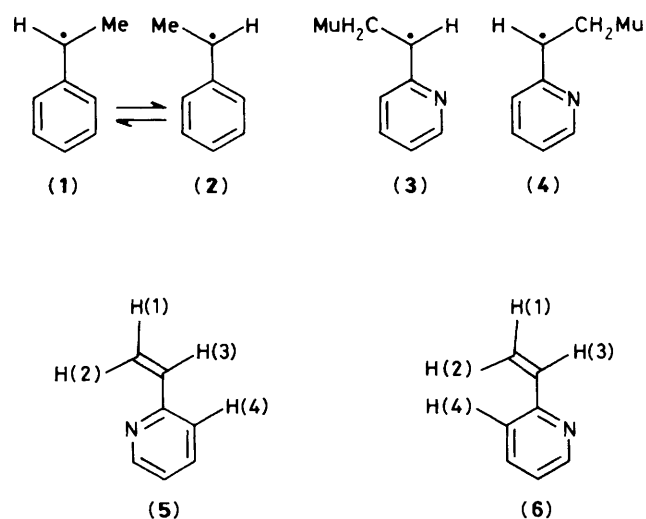
**Table 1.** Coupling constants for pyridylmethyl (pyridyl ethyl) radicals and the corresponding phenyl derivatives.

| Radical                               | Coupling <sup>a</sup> /G |
|---------------------------------------|--------------------------|
| PhCHCH <sub>2</sub> Mu <sup>b</sup>   | 24.00                    |
| 2-PyCHCH <sub>2</sub> Mu <sup>c</sup> | 25.18/25.58              |
| 4-PyCHCH <sub>2</sub> Mu <sup>c</sup> | 25.69                    |
| PhCH <sub>2</sub> <sup>d</sup>        | 16.35                    |
| 3-PyCH <sub>2</sub> <sup>d</sup>      | 16.51                    |
| 2-PyCH <sub>2</sub> <sup>d</sup>      | 16.88                    |
| 4-PyCH <sub>2</sub> <sup>d</sup>      | 17.20                    |

<sup>a</sup> 1G = 10<sup>-4</sup>T. <sup>b</sup> Ref. 9. <sup>c</sup> This work. <sup>d</sup> Ref. 2.

In this context, we were interested to make a kinetic determination of the radical-stabilising effect of a pyridyl group. An e.s.r. study<sup>3</sup> was made previously of the resonance stabilisation energies of some substituted benzyl radicals, from the linewidth alternation caused by isomerisation of the type (1)  $\rightleftharpoons$  (2). However, the e.s.r. spectra of pyridylmethyl radicals in solution are of low intensity because of their additional complexity,<sup>2</sup> and it would be very difficult to study linewidth effects similarly as a function of temperature.

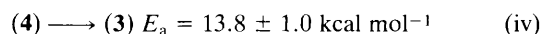
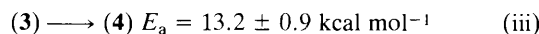
We decided instead to apply the muon spin rotation ( $\mu$  s.r.) technique<sup>4</sup> to this problem:  $\mu$  s.r. methods have been used previously to measure isomerisation rates in conjugated radicals.<sup>5</sup> Figure 1 shows the muon precession signals measured in a sample of 2-vinylpyridine during irradiation with a beam of spin-polarised muons at room temperature: signals for the isomers (3) and (4) are well resolved from one another and they are clearly present in different concentrations. (One advantage of the  $\mu$  s.r. technique is that the greater muon magnetic moment will result in a greater frequency difference between the hyperfine couplings of isomeric radicals, thereby giving an effectively higher resolution.) Since the ratio of concentrations of the two vinylpyridine isomers will be the same as the initial ratio of the two vinylpyridine isomers, we can assign the radicals by an n.m.r. determination of the composition of the 2-vinylpyridine.



The presence of two isomers [(5) and (6)] is most clearly seen from the resonances of H(2) and H(3), which show that the ratio of isomers is 58 : 42; in good agreement with this, the corresponding ratio of radical amplitudes is 57 : 43. A nuclear Overhauser effect difference spectrum [with irradiation at the frequency of H(4)] shows an enhancement in the H(2) resonance of peaks due to the minor isomer, which is therefore identified as (6). It is reasonable that (6) is the minor (less stable) isomer, because of the destabilising steric interaction between the vinyl group and H(4), which is not present in (5). Therefore, the major radical in the  $\mu$  s.r. spectrum is the isomer (4).

To determine the kinetic data, a series of 8  $\mu$  s.r. spectra was run at temperatures between 297 and 405 K. The linewidth parameter  $\lambda_w$  is the sum of the residual width  $\lambda_o$  and the line broadening due to a reaction<sup>5</sup> [equation (ii)], where  $\lambda_R = A \exp(-E/RT)$ . We can obtain  $\lambda_o$  from the width of the  $\mu$  s.r. lines at lower temperatures where (3)  $\rightleftharpoons$  (4) isomerisation is slow ( $\lambda_R$  is negligible). At higher temperatures, pronounced broadening of the lines occurs, from which we obtain activation energies given in (iii) and (iv) [using  $\log(A/s^{-1}) = 13.3$ , from (1)  $\rightleftharpoons$  (2),<sup>3</sup> which is close to the value of 13.2 predicted from transition state theory for a reaction with zero activation entropy at room temperature].

$$\lambda_w = \lambda_o + \lambda_R \quad (\text{ii})$$



A lower barrier for (3)  $\longrightarrow$  (4) might be expected, since (3) will be destabilised by a steric interaction between H(4) and the  $\text{CH}_2\text{Mu}$  group [similar to the destabilisation proposed for the parent vinylpyridine isomer (6)], but, within experimental error, the two values are the same, giving an average of 13.5 kcal mol<sup>-1</sup> which we take as a measure of the resonance stabilisation energy of the 2-pyridylmethyl radical.

By using the revised value for the 2-methylpyridine C-H bond dissociation energy obtained by Benson and O'Neal<sup>6</sup> in Nonhebel and Walton's correlation,<sup>7</sup> we would predict a value of 15.2 kcal mol<sup>-1</sup> for the barrier to rotation of the  $-\text{CH}_2$  group in the 2-pyridylmethyl radical, which is rather higher than we observe here. In fact, the methylpyridine C-H bond dissociation energy measurements<sup>6</sup> suggest that all three isomeric pyridylmethyl radicals are more stabilised than is

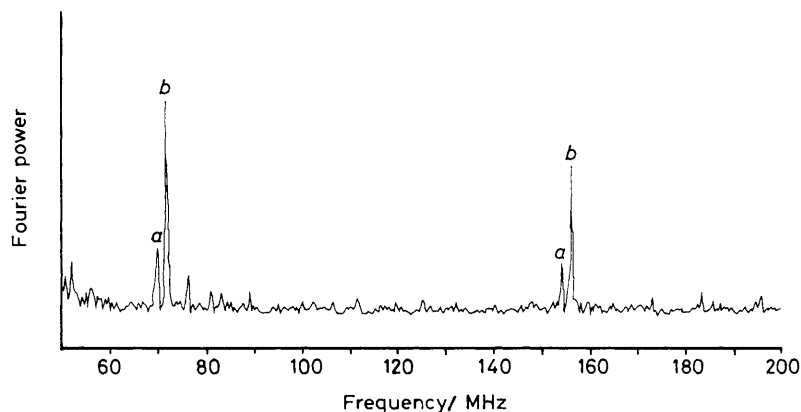


Figure 1. Muon precession signals observed during the irradiation of 2-vinylpyridine with spin-polarised, positive muons at room temperature, showing the presence of isomeric radicals *a* (3) and *b* (4).

benzyl. In contrast, the results from a study of  $\beta$ -C-C bond homolyses in the three isomeric ethylpyridines [ $DH^\circ$ -( $C_5H_4NCH_2-CH_3$ )] and in ethylbenzene by the 'very low pressure pyrolysis' technique<sup>8</sup> give the order of stabilities as: benzyl  $\sim 3- > 4- > 2$ -pyridylmethyl, although the order of 2- and 4-pyridylmethyl could be reversed within the errors quoted; thus these data are broadly in agreement with the couplings, which suggests that pyridylmethyl radicals are *less* delocalised than is benzyl. It appears that a redetermination of the C-H dissociation energies in the methylpyridines might prove worthwhile, since they seem too low as compared with that measured for toluene.<sup>6</sup>

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