^{13}C Nuclear Magnetic Resonance Studies on Aromatic Aldehydes. Torsional Barriers and Conformational Equilibria in Pyridinecarbaldehydes

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Low temperature ^{13}C n.m.r. has been used to study the barrier to internal rotation and the NO-*cis* : NO-*trans* population ratio in the three pyridinecarbaldehydes. The total bandshape analysis method was utilized, which resulted in *trans*-populations for pyridine-2- and -3-carbaldehyde of 0.94 and 0.80, respectively, at −123°. The results are compared with previous data obtained by other methods.

DURING the last few years efforts have been made to determine the conformational equilibria for the formyl group in pyridine-2- and -3-carbaldehyde. The long range spin coupling between the formyl proton and the aromatic protons *meta* to the formyl group has thus been used[1] as well as the dipole moment.[2] The drawback with both these methods is that only the mean value of some observable can be found, and no direct observation of the two conformers was possible. In such work it is therefore necessary to find the values for the observables from other experiments, often performed on model compounds. The values obtained are by necessity only approximate, and can easily cause serious errors in the conclusions.

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[1] (*a*) G. J. Karabatsos and F. M. Vane, *J. Amer. Chem. Soc.*, 1963, **85**, 3886; (*b*) M. R. Bramwell and E. W. Randall, *Spectrochimica Acta*, 1970, **26***A*, 1877; (*c*) W. Danchura, T. Schaefer, J. R. Rowbotham, and D. J. Wood, *Canad. J. Chem.*, 1974, **52**, 3986.

[2] (*a*) J. Barassin, *Ann. Chim. France*, 1963, **8**, 637; (*b*) J. Barassin, G. Queguiner, and H. Lumbroso, *Bull. Soc. chim. France*, 1967, 4707; (*c*) C. L. Chen and G. L. D. Ritchie, *J.C.S. Perkin II*, 1973, 1461.

Recently Galasso[3] reported results from INDO calculations on the stereochemistry of the pyridinecarbaldehydes. However, there are apparently no data available from direct measurement of the conformational equilibria in these compounds.

In order to avoid any assumptions regarding the individual conformers, a low temperature ^{13}C n.m.r. study of the pyridinecarbaldehydes has now been performed, in which the signals from the individual conformers could be directly observed. The torsional barrier for the formyl group has also been determined by means of a total bandshape analysis.

EXPERIMENTAL

Materials.—The pyridinecarbaldehydes were commercial products which were used with no purification, and no impurity signals could be detected by n.m.r. $CHCl_2F$ And CCl_2F_2 (1 : 1) were used as solvent. The samples were prepared by dissolving the aldehyde (2 mmol) in the solvent (2 g) directly in 10 mm n.m.r. tubes at −80°. The tubes were sealed off at liquid nitrogen temperature.

Apparatus.—All carbon-13 n.m.r. spectra were recorded on a Varian XL-100 spectrometer at 25.16 MHz operating in the Fourier transform mode. Typical settings for the Fourier transform parameters were: spectral width 2 000 Hz, acquisition time 2 s, pulse width 100 μs (flip angle 80°), and 1 000 transients. Proton noise decoupling and fluorine lock were used throughout this work. The temperature was measured by means of a thermocouple inserted in the normal 12 mm insert. Before use this thermocouple was calibrated against another inside a spinning dummy tube containing the same solvent as used in the subsequent experiments.

RESULTS

N.m.r. Spectra.—The ^{13}C chemical shifts for the three pyridinecarbaldehydes have been reported previously by Retcofsky and Friedel[4] and by Miyajima *et al.*[5] They both made the same assignment of the carbon-13 chemical shifts, which is also in agreement with the present results. In this work, an additional criterion for the assignment, the large chemical shift difference (*ca.* 200 Hz)[6] between the signals from the *ortho*-carbons *cis* and *trans* to the carbonyl oxygen, was used, resulting in the same assignment as found previously.[4,5]

According to the finding for some *ortho*- and *meta*-substituted benzaldehydes that the ^{13}C signal from the *ortho*-carbon *cis* to oxygen is shifted upfield *ca.* 8 p.p.m. compared with that for the *trans*-carbon,[6] the assignment of the signals from the two conformers was made as given in Table 1.

TABLE 1

^{13}C Chemical shifts in pyridinecarbaldehydes (in p.p.m. downfield from Me_4Si)

		Carbon				
	t/°C	2	3	4	5	6
4-Aldehyde	−80	151.5	123.5	141.4	123.5	151.5
	−165	151.1	119.2	140.8	127.1	151.8
3-Aldehyde	−80	152.7	131.3	136.8	124.4	156.0
NO-*trans*	−138	154.9	131.3	134.4	124.7	155.5
NO-*cis*	−138	148.4	130.7	141.1	124.7	154.9
2-Aldehyde	−80	152.3	121.9	137.5	128.4	150.3
NO-*trans*	−138	152.0	121.8	137.9	129.0	150.8
NO-*cis*	−138	152.0		137.9	129.0	150.8

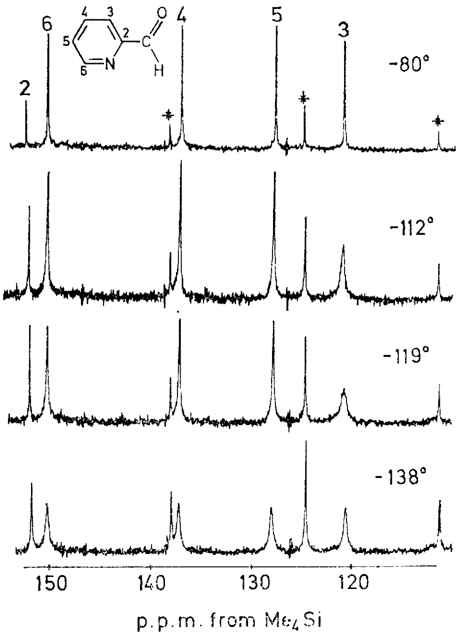

FIGURE 1 Aromatic carbon-13 n.m.r. spectrum from pyridine-2-carbaldehyde in $CHCl_2F$–CCl_2F_2 solution at low temperatures. The asterisked signals are due to CCl_2F_2. The change in the line intensities with temperature is due to the shortening of T_1 with decreasing temperature

Torsional Barriers and Conformational Equilibria.—Total bandshape analysis of the carbon-13 n.m.r. signals from the aromatic carbons was utilized to obtain both the torsional barrier for the formyl group and the populations of the two conformers. The exchange between the two conformers is a simple two-site process. When carbon-13 with complete proton decoupling is used, there is a pairwise coalescence of single lines, which is easily simulated with the aid of McConnell's equation.[7] The exchange rates at various temperatures were obtained by visual fitting of calculated to experimental bandshapes. For pyridine-4-carbaldehyde only the 3- and 5-carbon signals were used, even though the 2- and 6-carbon signals also showed non-equivalence. For the 3-carbaldehyde all signals except that from the 5-carbon showed non-equivalence and were used in the bandshape analysis. For the 2-carbaldehyde, only the 3-carbon signal could be used in the bandshape analysis. It is necessary to discuss the calculations for this case in more detail since the signal from the less populated conformer could not be observed (see Figure 1). At low temperature (slow exchange) it is sufficient to use the shape of the signal from the more populated conformer to determine the exchange rate,

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[3] V. Galasso, *Mol. Phys.*, 1973, **26**, 81.

[4] H. L. Retcofsky and R. A. Friedel, *J. Phys. Chem.*, 1967, **71**, 3592; 1968, **72**, 290; 1968, **72**, 2619.

[5] G. Miyajima, Y. Sasaki, and M. Suzuki, *Chem. and Pharm. Bull.* (*Japan*), 1972, **20**, 429.

[6] T. Drakenberg, R. Jost, and J. M. Sommer, *J.C.S. Perkin II*, 1975, 1682.

[7] H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 430.

since this shape is independent of the population as long as there is no overlap between the two signals. Even though the signal from the less populated conformer of pyridine-2-carbaldehyde could not be found, the variation of the chemical shift of the main signal with temperature was used to decide whether the missing signal should be located on the high or low field side of the main signal. As shown in Figure 2 the signal due to the 3-carbon shifts upfield when the temperature is lowered through the temperature region where line broadening occurred, showing that the missing signal must be downfield from the main signal. The use of the displacement of the main signal, 15 Hz, and the assumption of a chemical shift difference between the *ortho*-carbon signals from the NO-*cis*- and NO-*trans*-conformers of 8 p.p.m. as found in benzaldehydes give a population of 7% of the NO-*cis*-conformer. The chemical shift difference for the 6-carbon signals in *o*-methylbenzaldehyde, 11 p.p.m., indicates that a larger shift difference might be also obtained for pyridine-2-carbaldehyde, which should result in a lower population of the NO-*cis*-conformer, but even for a chemical shift difference of 12 p.p.m. the calculated NO-*cis*-population is 5%.

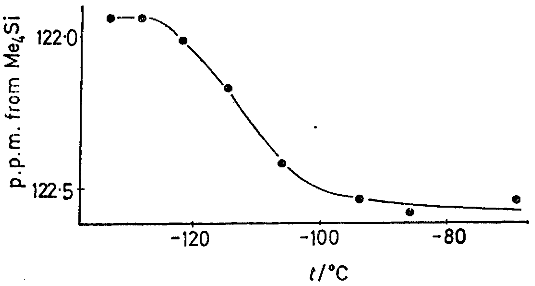

FIGURE 2 Change in the chemical shift of the 3-carbon signal in pyridine-2-carbaldehyde as a function of temperature

The dominant conformer is found to be NO-*trans* for both pyridine-2- and -3-carbaldehyde and the population ratios as well as the free energy of activation are given in Table 2.

TABLE 2

Free energy (kJ mol^{-1}) of activation for the hindered rotation and population ratios in pyridinecarbaldehydes

	$\Delta G^{\ddagger}_{150\ \mathrm{K}}$	*trans* : *cis*	$\Delta G^{0}_{150\ \mathrm{K}}$	$V^*/4$ [a]
4-Aldehyde	24.7 ± 1	1	0	15.9
3-Aldehyde	30.1 ± 1	4	1.55 ± 0.2	19.2
2-Aldehyde	31.4 ± 1	16	3.6 ± 0.5	19.7

[a] Gas phase.[8]

Only for the 3-carbaldehyde was it possible to perform a bandshape analysis of such quality to make an evaluation of activation enthalpy and entropy from a plot of $\ln(T\tau)$ against $1/T$ meaningful, resulting in the following values: $\Delta H^{\ddagger}$ 30 ± 2 kJ mol^{-1} and $\Delta S^{\ddagger}$ -4 ± 10 J mol^{-1} K^{-1}, where the errors include both statistical and estimated systematic errors from uncertainties in temperature and relaxation time, T_2.

DISCUSSION

Torsional Barriers.—The torsional barriers in the three pyridinecarbaldehydes have previously been estimated from far i.r. spectra by Miller *et al.*,[8] but it has been demonstrated several times that it is difficult to obtain accurate data on activation energies by this method.[9] In this case, it also appears that the i.r. data are consistently *ca.* 10 kJ mol^{-1} lower than the present activation energies derived from n.m.r. bandshape analysis. It should, however, be pointed out that the i.r. data were obtained from the gas phase, whereas the n.m.r. data were obtained from solutions. Miller *et al.*[8] also give a value (only for comparison) for the activation energy in pyridine-4-carbaldehyde in solution (25.1 kJ mol^{-1}) that is in excellent agreement with the present value (24.7 kJ mol^{-1}). Also the difference between the 4- and the 2- and 3-carbaldehydes obtained from the two methods is very similar, with the pyridine-4-carbaldehyde barrier *ca.* 6 kJ mol^{-1} lower than the others. This is in agreement with the widely accepted idea that the resonance effect from a substituent on a benzene ring is most pronounced at the *para*-position. The nitrogen in the pyridine ring can be compared to a strongly electron-attracting substituent, like nitro or formyl, and should thus induce a decrease in the barrier to formyl rotation compared with that in benzaldehyde, which is what is found (for benzaldehyde[10] $\Delta G^{\ddagger}$ 31.8 kJ mol^{-1}). The small difference between the 2- and 3-carbaldehydes is also in complete agreement with results for *ortho*- and *meta*-substituted benzaldehydes.[6]

Conformational Equilibria.—Danchura *et al.*[1c] have given a thorough discussion of the conformational equilibria in pyridine-2- and -3-carbaldehyde as a function of solvent polarity based on data obtained from measured stereospecific long-range spin–spin couplings and from INDO calculations. Their data for pyridine-3-carbaldehyde are in good agreement with the present value for the population ratio and this also agrees well with a recent value obtained from the observed dipole moment and Kerr constant.[2c] The agreement for pyridine-2-carbaldehyde is less satisfactory. The energy difference between the two conformers derived from observed long-range spin couplings is critically dependent on the assumed values for the stereospecific long-range coupling constants, which in this case could not be measured directly.[1c] If the value for $^5J^{\mathrm{CHO,H}}$ in pyridine-2-carbaldehyde is increased by *ca.* 10%, which is not unreasonable, an NO-*trans* : NO-*cis* population ratio in better agreement with that found in the present study would be obtained.

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