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Restricted Rotation about the C–N Bond in 1-Acylpyrroles

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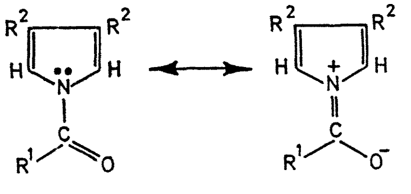
Nuclear magnetic resonance studies have shown the presence of restricted rotation about the C–N bond in dimethylformamide and its analogues.[1] The barrier to internal rotation of this type has generally been ascribed to the partial double-bond character of the C–N bond of the amide group. The C–N bond of 1-acylpyrroles is also expected to possess double-bond character, as shown by the following canonical structures. Since the ionization potential of pyrrole (8·97 ev) is close to that of dimethylamine (8·93 ev),[2] the ionic structure of 1-acrylpyrroles may be as important as that of dimethylformamide.

Restricted rotation in 1-acylpyrroles has now been studied by n.m.r. spectroscopy. The 1-acylpyrroles investigated give either A_2B_2 (for I, II, III) or A_2 (for IV) patterns when the spectra are measured at 40°. In other words, the internal rotation about the C–N bond at this temperature is fast on the n.m.r. time scale. As the temperature is lowered, the signals of the protons at the C-2 and C-5 positions are generally split into two groups (Figure). No appreciable change is observed in signals due to protons at C-3 and C-4. These observations indicate that the internal rotation is strongly restricted at low temperature. When the internal rotation is very slow on the n.m.r. time scale, the two peaks due to the protons at C-2 and C-5 are separated by approximately 20 Hz. The value is reasonable if the carbonyl group is coplanar with the plane of the pyrryl group. In this case, the signals at higher field may be assigned to the proton (H_a) closer to the oxygen atom of the carbonyl group. The final peak separations (Δν) and coalescence temperatures (T_c) are summarized in the Table, and the free energies of activation ($\Delta F_c^\ddagger$) at T_c (roughly estimated) are also shown.



(I) $R^1=R^2=H$
(II) $R^1=Me, R^2=H$
(III) $R^1=Ph, R^2=H$
(IV) $R^1=R^2=Me$

The values for T_c and $\Delta F_c^\ddagger$ for the above compounds are considerably lower than those for *NN*-dimethylformamide analogues with a corresponding acyl group ($R^1C{=}O$); *i.e.*, the internal rotation about the C–N bond is less hindered. Presumably, the double-bond character of the C–N bond in the former compounds may be less than in the latter. It is noteworthy that the coalescence temperatures are in the following order of acyl groups: formyl > acetyl > benzoyl. The same trend is observed in the corresponding *NN*-dialkylamides. A part of the substituent effects may

Spectral data for the restricted rotations in 1-*acylpyrroles*[a]

Compound	Δν (Hz.)	T_c	Estimated $\Delta F_c^\ddagger$ (kcal./mole)
(I)	21·0±0·5	5±1	14
(II)	22·9±0·5	−28±1	13
(III)	—	<−70	—
(IV)	24·7±0·5	−5±1	14

[a] Measured at 60 MHz. (Varian A-60 spectrometer); $CDCl_3$ solution.

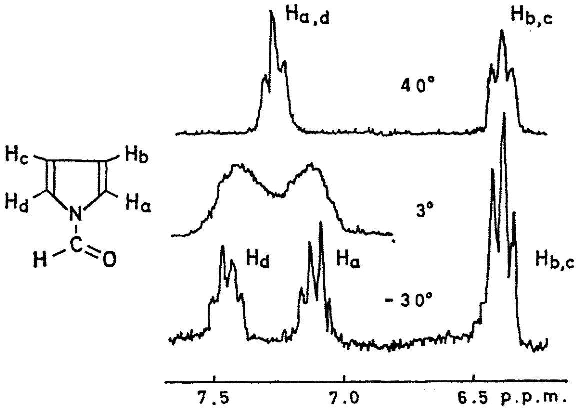


Figure. *Effect of temperature on the ring proton signals of* 1-*formylpyrrole* ($CDCl_3$ *solution*). *The chemical shifts are measured from the internal* Me_4Si *reference signal.*

be due to the decrease in the electronegativity of the carbonyl groups when the substituent (R^1) is donating electrons either by inductive or by electromeric effect. In addition, appreciable steric hindrance exists if 1-benzoylpyrrole (III) tries to adopt a completely planar conformation, since the van der Waals radius of the proton at the pyrryl 2- or 5-position overlaps with that of the proton at the 2′- or 6′-position. This steric hindrance is expected to raise the valley of the potential-energy curve for the internal rotation. Accordingly, the coalescence temperature for 1-benzoylpyrrole is much lower than those for other 1-acylpyrroles. The coalescence temperature for 1-acetyl-3,4-dimethylpyrrole (IV) is higher than that for 1-acetylpyrrole by as much as 20°. As a consequence of methyl substitution, the ionization potential of the pyrryl group is lowered and the double-bond character of the C–N bond under investigation will be increased. The increased double-bond character certainly raises the barrier to internal rotation. In addition, it is possible that some other factors, such as solvation, may also play auxiliary roles in determining the coalescence temperature.

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[1] R. C. Neuman, jun., and V. Jonas, *J. Amer. Chem. Soc.*, 1968, **90**, 1970, and references quoted therein.

[2] I. Omura, H. Baba, and K. Higashi, *J. Phys. Soc. Japan*, 1955, **10**, 317; J. Collin, *Canad. J. Chem.*, 1959, **37**, 1053.