The Barrier to Internal Rotation in Benzaldehydes. A ^{13}C Nuclear Magnetic Resonance Study

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Summary The barrier to rotation around the phenyl-carbonyl carbon bond in a series of substituted benzaldehydes has been measured by a dynamic n.m.r. method using ^{13}C Fourier transform technique and a mixture of low-melting solvents.

RECENTLY many studies of rotation about a σ-bond possessing some π-character have been reported.[1] Benzaldehyde is one of the best model compounds, as the π-character of the phenyl–carbonyl carbon bond can be modified by varying the substituents on the aromatic ring. This permits a comparison of the barrier with other parameters already known for these molecules (*e.g.* basicities, σ^+ constants of the substituents, ^1H and ^{13}C chemical shifts). However, because of the small difference in chemical shifts of the magnetically non-equivalent nuclei, the low value of the torsional barrier ($\Delta G^\ddagger < 45$ kJ mol^{-1}), and the low solubility in low-melting solvents work has been limited to *p*-dimethylamino- and *p*-methoxy-benzaldehydes.[2]

We now report the barrier to internal rotation in a series of benzaldehydes obtained using ^{13}C F.T. n.m.r. spectroscopy and complete lineshape analysis. The main advantage of the ^{13}C spectrum in substituted benzaldehydes is the large chemical shift difference of the non-equivalent *ortho* (200 Hz) and *meta*-carbons (10—50 Hz) compared with the

TABLE

Substituent	$\Delta G_{Tc}^\ddagger$ /kJ mol^{-1}	T_c/°C
NMe_2[a]	44·3	−40
OMe[b]	36·4	−80
Me[b]	34·3	−90
$CHMe_2$[b]	32·6	−100
Cl[b]	32·6	−100
H[b]	31·8	−105
CF_3[b]	28·5	−120

[a] Measured by complete bandshape analysis: $\Delta H^\ddagger = 46{\cdot}0$ kJ mol^{-1}; $\Delta S^\ddagger = +\ 7{\cdot}1$ J mol^{-1} K^{-1}. [b] Calculated from Eyrings equation at coalescence, T_c.

non-equivalent *ortho*-protons (6 Hz) and *meta*-protons (1 Hz). When broad band proton-decoupling is used very simple spectra are obtained. The use of a mixture of freons, $CHCl_2F$ and CCl_2F_2, allowed us to record spectra at temperatures as low as −165 °C with an aldehyde concentration of 0·5 M. For *p*-dimethylaminobenzaldehyde complete bandshape calculations were performed on *ortho*- as well as on *meta*-carbon signals, but for the other benzaldehydes only the coalescence of the *ortho*-carbon signals was studied. Values of the barrier to internal rotation of a series of *p*-substituted benzaldehydes are shown in the Table. The obtained $\Delta G^{\ddagger}$ values show a good correlation with the Brown σ^+ constants of the *para*-substituents as has been shown in complexed and protonated benzaldehydes.[3] The present data are in very close agreement with previously reported values estimated by n.m.r.,[2] but are different from those found from i.r. and microwave studies.[4]

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