Barriers to Internal Rotation in Benzoyl Cyanide and Benzoyl Halides

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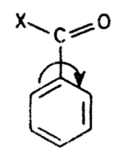
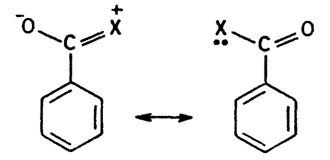
Summary The free energy barriers ($\Delta G^{\ddagger}$) in benzoyl cyanide, fluoride, chloride, and bromide, as determined by ^{13}C dynamic n.m.r. spectroscopy, are 8·4, 7·0, 6·4, and 6·1 kcal mol^{-1}, respectively.

Barriers to internal rotation about the carbonyl–aromatic bonds in aromatic aldehydes and ketones and their protonated derivatives and Lewis acid complexes have been extensively studied by both ^{1}H and ^{13}C n.m.r. spectroscopy.[1,2] There seems, however, to be almost no data on such barriers in compounds of the type Ar–CO–X (except when Ar is *p*-methoxyphenyl and X is chlorine[3]), where X is a halogen or pseudohalogen, or where X is a group which is bonded to the carbonyl carbon by a heteroatom. It seemed to us that substantial barriers to internal rotation should exist when X is a halide or a pseudohalide such as CN. This is in fact the case, as shown by low temperature ^{13}C n.m.r. spectroscopy of the compounds given in the Table.

Benzoyl cyanide (**1**) has the highest barrier to internal rotation of the compounds studied. This is understandable, since the cyano group is strongly electron attracting by its inductive (or field) effect, and it does not donate electrons by a resonance effect. The barriers in the benzoyl halides, (**2**), (**3**), and (**4**), are about halfway between those of benzaldehyde (7·5 kcal mol^{-1}) and acetophenone (5·3 kcal mol^{-1}). The halides have lone pairs of electrons which can enter into a resonance interaction with the carbonyl group, as in (**6a**) and (**6b**), thus competing with the π electrons of the aromatic ring and thereby lowering the barrier to internal rotation. This is partly offset by the electron attracting inductive effects of the halogens, particularly in the case of fluorine.



(1) X=CN (4) X=Br
(2) X=F (5) X=OMe
(3) X=Cl



(6a) (6b)

Table. N.m.r. parameters and free energy barriers.

Compound[a]	Chemical shifts[b] of *ortho* carbons at low temperature	Coalescence temperature T_c,/°C	$\Delta G^{\ddagger}$/kcal mol^{-1} [d]
(1)	128·2, 133·6	−85° ± 2	8·4 ± 0·1
(2)	131·8, 132·9[c]	−126° ± 2	7·0 ± 0·1
(3)	130·3, 134·0	−130° ± 2	6·4 ± 0·1
(4)	130·0, 136·0	−135° ± 2	6·1 ± 0·1

[a] In $CHFCl_2:CHF_2Cl$ (1:3) + 5% $(CD_3)_2CO$. [b] Measured on a Bruker WP-200 spectrometer at 50·32 MHz (protons decoupled) at 20 °C or more below T_c; shifts are given in p.p.m. from Me_4Si and the order of the numbers does not imply a chemical shift assignment. [c] $^{3}J(^{13}C-^{19}F) = 9$ Hz. [d] 1 cal = 4·184 J.

A nematic phase n.m.r. study of (**2**) at room temperature has shown that this molecule is planar and that the barrier to internal rotation is greater than 7 kcal mol^{-1}.[4] The latter deduction, although requiring an assumption about the shape of the potential function for internal rotation, is in reasonable accord with the presently determined barrier, especially when the differences in solvents and temperatures of the two experiments are considered. A microwave study of (**2**) has given a lower barrier ($4{\cdot}5 \pm 0{\cdot}5$ kcal mol^{-1}),[5] but this is to be expected because this result refers to the gas rather than to the solution phase.[4] The barrier in (**3**) is 1·3 kcal mol^{-1} lower than that in the *p*-methoxy derivative of this compound,[3] a difference which is very similar to that (1·4 kcal mol^{-1}) in the corresponding aldehyde system ($X = H$).[1,2]

We have measured the ^{13}C n.m.r. spectrum of methyl benzoate (**5**) down to −175 °C, but no dynamic n.m.r. effect was observed. This negative result is consistent with a low barrier to internal rotation, but it could also result from a very small chemical shift difference between the *ortho* carbons, since these atoms are flanked by similar oxygen functions. The barrier in ethyl *p*-methoxybenzoate has also been found to be too low ($< 4{\cdot}8$ kcal mol^{-1}) for measurement by dynamic n.m.r. methods.[3]

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[1] For a review, see S. Sternhell, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' ed. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 163.

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[3] T. Drakenberg, J. Sommer, and R. Jost, to be published.

[4] T. C. Wong and E. E. Burnell, *J. Magnetic Resonance*, 1976, **22**, 227.

[5] R. K. Kakar, *J. Chem. Phys.*, 1972, **56**, 1189. It is also possible, as suggested by a referee, that the barrier height obtained by microwave may err on the low side, as this method is not free of assumptions when the barrier is relatively high.