Nuclear Magnetic Resonance Studies on Benzaldehydes. Part II.† Carbon-13 Nuclear Magnetic Resonance Studies of the Barrier to Internal Rotation and the Conformational Equilibrium in *o*- and *m*-Substituted Benzaldehydes

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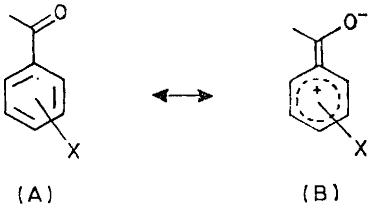
The *O-cis* : *O-trans* population ratio of several unsymmetrically substituted benzaldehydes has been measured by means of ^{13}C Fourier transform n.m.r. spectroscopy at −150°, where the *O-cis–O-trans* exchange is frozen out. The barrier to internal rotation about the phenyl–formyl bond was estimated by application of dynamic n.m.r. methods to the ^{13}C spectra at *ca.* −120°. $\Delta G^{\ddagger}$ Values are *ca.* 30 kJ mol^{-1}.

ROTATIONAL isomerism in *o*- and *m*-substituted benzaldehydes has recently been investigated by various techniques, dipole moment measurements,[1-5] i.r.,[6-8] and ^{1}H and ^{19}F n.m.r. spectroscopy.[9-11] However with none of these methods is it possible to measure the relative populations directly, and the agreement among the data reported is poor, especially for *m*-substituted benzaldehydes. There is also an INDO calculation available,[10] which gives a slightly lower energy for the *O-trans*-rotamer than for the *O-cis*-rotamer in *m*-fluorobenzaldehyde.

The barrier to internal rotation in benzaldehydes originates from the π-electron delocalisation from the ring to the electron deficient carbonyl carbon atom as shown by the mesomeric forms (A) and (B).



Normally n.m.r. is a very powerful tool in studies of isomerism of this type. The energy barrier to interconversion of the two rotamers must, however, be reasonably high in order to make it feasible to study the isomers under slow exchange conditions. The torsional barrier in benzaldehydes with no strong electron-donating group in the *para*-position is <35 kJ mol^{-1} and is not easily studied with ^{1}H n.m.r. We have, however, recently shown that barriers of this magnitude are relatively easy to measure by means of proton noise decoupled ^{13}C n.m.r. spectroscopy.[12]

In this paper we report the direct observation of the two conformers of some *o*- and *m*-substituted benzaldehydes at −150° in Freon mixture ($CHCl_2F$–CCl_2F_2) by ^{13}C Fourier transform n.m.r. spectroscopy, as well as the determination of the height of the torsional barrier.

RESULTS AND DISCUSSION

^{13}C *Chemical Shifts*.—At ambient temperature with proton noise decoupling, singlet ^{13}C n.m.r. lines are observed for all the carbons in both 2- and 3-substituted benzaldehydes (except for doubling due to fluorine coupling). The assignment of these signals is not straightforward, as the normal substituent shift parameters can not be used as long as the *cis* : *trans* population ratio is not known. As has been shown in previous work on *para*-substituted benzaldehydes the shifts for the carbons *ortho* to the aldehyde group can differ by *ca.* 10 p.p.m. between the *cis*- and *trans*-rotamers.[12]

When the temperature is lowered below −100° some of the ^{13}C signals start broadening and at −150°, for most of the compounds, two well resolved sets of signals evolve. For 2-fluoro- and 2-chloro-benzaldehydes only one set of signals was observed at all temperatures, indicating that these compounds are exclusively in one conformer. Dipole moments[5] and ^{1}H n.m.r. data[10] show that these two aldehydes exist mainly as the *O-trans*-rotamer and indeed this is also in agreement with our ^{13}C data.

The chemical shift assignment was primarily based on the substituent effects derived from *para*-substituted benzaldehydes[12] (Table 1). These increments show some small differences compared with those available in the literature.[13,14] The assumption that the 2-fluoro- and 2-chloro-benzaldehydes exist mainly as the *O-trans*-

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† Part I, ref. 12.

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conformer makes it possible to differentiate between C-2 and -6 signals from the two conformers in the other benzaldehydes: the signal from the carbon atom *cis* to oxygen appears *ca.* 10 p.p.m. to higher field than the other. The fact that carbon atoms bearing no protons normally have longer relaxation times than proton-bearing atoms was also helpful in the assignment of the signals from substituted carbons.

TABLE 1

^{13}C Chemical shift substituent effect in monosubstituted benzaldehydes

Substituent	C-1	*ortho*	*meta*	*para*
CH_3	+10.9	+0.7	−0.1	−2.2
F	+32.0	−12.7	+2.4	−3.3
Cl	+6.4	+0.5	+1.1	−1.7
Br	−4.8	+3.4	+1.1	−1.2

TABLE 2

^{13}C Chemical shifts of unsymmetrically substituted benzaldehydes at −150° (in p.p.m. for external Me_4Si)

		Carbon							
Aldehyde	Conformer	C=O	C-1	C-2	C-3	C-4	C-5	C-6	Other
o-CH_3	*O-cis*	193.2		140.4		134.0		137.2	21.2
			137.0		130.0	or	126.4		
	O-trans	196.8		142.4		135.1		126.4	17.6
o-F	*O-trans*	189.2	122.8	165.4	116.6	137.5	124.8	127.4	
m-CH_3	*O-cis*		136.1	125.8				131.5	
		195.0	or		139.2	135.4	128.0		20.0
	O-trans		135.8	135.2				122.6	
m-F	*O-cis*			111.4		122.1	131.5	130.3	
		193.7	137.4		162.6				
	O-trans			120.2		122.6	131.2	121.7	
m-Cl	*O-cis*			125.2				132.0	
		193.0	136.2		134.4	134.6	130.2		
	O-trans			133.6				123.6	
m-Br	*O-cis*			128.6	122.5			132.8	
		193.4	136.9		or	137.6	130.5		
	O-trans			134.5	123.4			124.6	

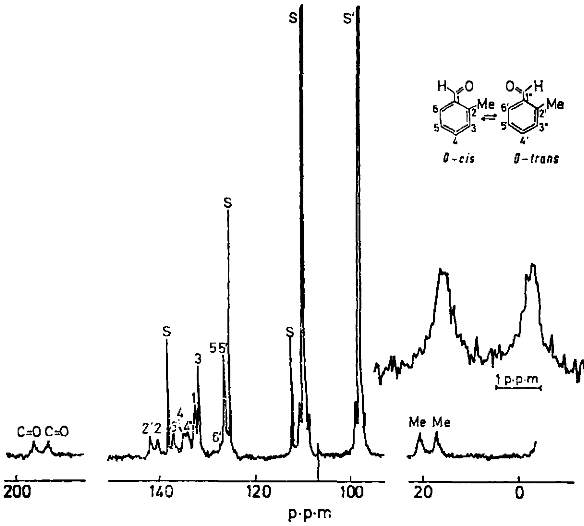
A comparison of calculated chemical shifts, by means of the data in Table 1, and experimental values, given in Table 2, generally show a very good agreement (within 1 p.p.m.), whereas a reversed assignment of the signals from the *O-cis* and *O-trans*-rotamers do not. Thus it was possible to make an unambiguous assignment of the non-equivalent C-2 and -6 signals to the *O-cis*- and *O-trans*-rotamers, respectively.

In some cases also C-1 and -3 to -5 showed non-equivalent signals, but due to the small chemical shift differences, assignment to the *O-cis*- and *O-trans*-conformers could not always be made (see Table 2).

Rotational Isomerism.—ortho-*Substituted benzaldehydes.* As mentioned above 2-fluoro- and 2-chloro-benzaldehydes exist mainly in the *O-trans*-configuration and only one set of carbon-13 signals was observed. This is believed to be due to the repulsive dipole–dipole interaction between the halogen and the oxygen in the *O-cis*-rotamer. In the *o*-tolualdehyde, (Figure) however, the *O-cis* : *O-trans* population ratio is close to unity, which is understandable since there is no strong dipolar interaction in this molecule (see later).

meta-*Substituted benzaldehydes.* For all the *m*-benzaldehydes studied both rotamers were present in detectable amounts as judged from ^{13}C n.m.r. spectra at −150° (Table 3). In these molecules there is no strong interaction between the formyl group and the other substituent, and the energy difference between the two rotamers is expected to be small. Intuitively one might expect the *O-trans*-rotamer to be slightly stabilized compared to the *O-cis* in non-polar solvents due to the smaller dipole moment of the former.

INDO Calculations [10] on *m*-fluorobenzaldehyde have given an energy difference of 0.16 kcal mol^{-1}, with *O-trans* more stable, and ^{1}H long-range couplings, for the same molecule, indicate a population ratio close to one. Our ^{13}C n.m.r. data is, however, best interpreted by the *O-cis*-rotamer being more stable and the population ratio approaches unity when the polarity of the *m*-substituent decreases. If we accept that *o*-chlorobenzaldehyde adopts mainly the *O-trans*-conformation, the only necessary assumption to make an unambiguous assignment of the two sets of signals to the two rotamers is that the shielding–deshielding effect of the carbonyl group on the unsubstituted *ortho*-carbons is similar in



^{13}C N.m.r. spectrum of *o*-tolualdehyde at −145° in CCl_2F_2 (S)–$CHFCl_2$ (S′)

ortho- and *meta*-substituted benzaldehydes, a reasonable assumption.

The observed population ratios might be rationalized in terms of a hydrogen-bond type interaction between the slightly positive *o*-protons and the carbonyl oxygen. This interaction should be a little stronger in the *O-cis*-rotamer since one *o*-proton may be more positive than the other owing to the inductive effect of the *m*-substituent. This should explain why the *O-cis* population decreases as observed: F > Cl > Br > Me. An alternative and complementary explanation is afforded by dipole–dipole repulsion in the *O-trans*-form between the C-2–H and the formyl C–H bonds.

TABLE 3

Torsional barriers and *O-trans* populations at −150°

Benzaldehyde substituent	*O-trans* Population	$\Delta G^{\ddagger}$/kJ mol^{-1} (± 1.0)
o-CH_3	0.50	27.0
o-F	1.00	
o-Cl	1.00	
m-CH_3	0.45	33.0
m-F	0.26	30.7
m-Cl	0.35	31.9
m-Br	0.41	33.0

Barrier to Internal Rotation.—The rate of rotation of the formyl group has been estimated from the carbon-13 n.m.r. spectra at temperatures of *ca.* −120°, where an appreciable broadening of the lines due to exchange was observed.

The evaluation of the rate constants was performed by a visual fitting of calculated to experimental spectra. The free energies of activation were then calculated by means of the Eyring equation, and are collected in Table 3.

We note that the torsional barrier for the *m*-substituted benzaldehydes decreases slightly with the increasing mesomeric π-electron releasing ability of the halogens. *m*-Tolualdehyde has approximately the same barrier as *p*-tolualdehyde [12] (34.3 kJ mol^{-1}), whereas *o*-tolualdehyde shows a small but non-negligible decrease of the barrier height (*ca.* 6 kJ mol^{-1}) which is probably due to steric interaction between the methyl and the formyl groups. The most surprising point here is that the methyl-proton and -oxygen interactions seem essentially the same as judged from the equal population of the two rotamers.

EXPERIMENTAL

The substituted benzaldehydes were commercially available and were used without further purification.

The samples were prepared directly in 10 mm n.m.r. tubes by dissolving the benzaldehydes at dry-ice temperature in a mixture of CCl_2F_2 and $CHCl_2F$, as 0.5M solutions. These samples were used only for low temperatures and were not sealed.

All spectra were recorded on a Varian XL-100-15 n.m.r. spectrometer in the Fourier transform mode, with typical settings as follows: spectral width 5 000 Hz, aquisition time 2 s, pulse width 80 μs, and 1 000 transients. Proton noise decoupling was used throughout this work.

The temperature was measured by means of a copper–constantan thermocouple fixed inside the 12 mm insert. This thermocouple was calibrated against another one inside a spinning 10 mm n.m.r. tube with the Freon mixture used for the samples.

Theoretical bandshapes were calculated on a Hewlett–Packard desk calculator equipped with a plotter. The rate constants were calculated at two different temperatures (−120 and −90°) where the line shape is very sensitive to variations in the exchange rate. The bandshape analysis for these simple systems has been described earlier.[15]

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