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CARBONYL C^{13} CHEMICAL SHIFTS IN SUBSTITUTED BENZALDEHYDES

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Abstract—The carbonyl C^{13} chemical shifts in some substituted benzaldehydes have been measured by the "indirect" method using heteronuclear double resonance techniques on the C^{13} satellites in the 100 Mc/s proton spectra. The chemical shift changes can be explained largely by the influence of the substituent on the conjugation between the carbonyl group and the aromatic ring, although this can cause different effects to be observed for *ortho*-, *meta*- and *para*-positions of substitution. The results for the substituted benzaldehydes are compared with those obtained by other workers on the changes in chemical shift produced by substituents in other aromatic systems.

C^{13} CHEMICAL shifts can be obtained in two main ways: by direct observation on an NMR spectrometer operating at the C^{13} resonant frequency (10·705 Mc/s at 10 kilogauss) or by indirect observation using double resonance techniques on the C^{13} satellites present in the proton NMR spectra of organic compounds. The low natural abundance of C^{13} nuclei (only 1·1%) and the fact that the C^{13} magnetic moment is about four times less than that of H^1 combine to make the direct observation of C^{13} resonances considerably more difficult than in the proton case. The signal strength from a given number of carbon atoms is only $1{\cdot}76 \times 10^{-4}$ of that from the same number of protons in the same magnetic field and specialized techniques[1,2] are required to overcome this decrease.

In the indirect method the C^{13} satellites in the proton spectrum are only 180 times smaller than the main proton peak and hence a gain of about 30 in sensitivity should exist between the indirect and direct methods of measuring C^{13} chemical shifts in natural abundance. If the C^{13} nucleus under consideration is coupled to more than one proton, e.g. in a methyl group, then the gain is even greater for the indirect method. However, the indirect method suffers in that it is restricted, of course, to those C^{13} nuclei carrying protons.

Stothers and Lauterbur[3] have measured C^{13} chemical shifts in various types of organic carbonyl groups, including some substituted benzaldehydes, by direct observation. In the present work, more substituted benzaldehydes have been examined by the indirect method using the C^{13} satellites of the formyl proton.

Experimental detail and results. The Varian HR. 100 spectrometer used in this work utilises a modified probe in which the transmitter coil generates both the 100 Mc/s proton frequency and the 25·14 Mc/s C^{13} resonance decoupling frequency. Full details of the principles of the method, the apparatus, and the experimental procedure have already been given.[4] Theoretical reviews of double resonance are also

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[1] P. C. Lauterbur, *Ann. N.Y. Acad. Sci.* **70**, 841 (1958).

[2] P. C. Lauterbur, *J. Amer. Chem. Soc.* **83**, 1838 (1961).

[3] J. B. Stothers and P. C. Lauterbur, *Canad. J. Chem.* **42**, 1563 (1964).

[4] J. H. Allen, J. K. Becconsall and D. W. Turner, *J. Sci. Inst.* **41**, 673 (1964).

available.[5,6] Samples containing C^{13} in natural abundance were examined in 5 mm OD sample tubes spun in the normal way. Neat liquids were used whenever possible; otherwise saturated solutions were prepared in appropriate solvents. Tetramethylsilane was added to the samples and was used as a reference for both the H^1 and C^{13} chemical shifts.[4] The C^{13} chemical shift measurements could be made within a few minutes of recording the normal proton spectrum without removing the sample from the instrument.

The C^{13} resonance frequencies actually measured in the indirect method are those at the magnetic field at which the protons in TMS resonate at 100 Mc/s. The C^{13} resonance frequency of benzene was also measured under these conditions in order to facilitate comparison with other published results. The C^{13} resonance frequencies can be measured to ±2 c/s which gives an accuracy of ±0·08 ppm for the chemical shifts. Table 1 shows the carbonyl C^{13} and formyl H^1 chemical shifts in some mono-substituted benzaldehydes. Column 2 gives the carbonyl C^{13} shifts measured by the indirect method in ppm relative to benzene. In column 3 the direct observation results of Stothers and Lauterbur[3] are given. These last results were obtained relative to an external standard of CS_2 and are judged to be accurate to ±0·5ppm. For convenience, the value of −65·0 ppm for the chemical shift of CS_2 relative to benzene[2] has been used to convert these results to the benzene scale. Column 4 shows the formyl H^1 chemical shifts in ppm relative to TMS. For those compounds examined by the indirect method the H^1 and C^{13} chemical shift measurements were made on the same sample. For the compounds examined by Stothers and Lauterbur, the formyl H^1 chemical shifts have been taken from the data of Klinck and Stothers.[7] These values (given in parenthesis

TABLE 1. CARBONYL C^{13} AND FORMYL H^1 CHEMICAL SHIFTS IN SUBSTITUTED BENZALDEHYDES

Substituent	C^{13} (in ppm from C_6H_6)		H^1 in ppm from TMS	Remarks on C^{13} measurements
	This work	Ref. 3		
H	−63·75	−63·2	−9.972	neat
o-Cl	−60·61		−10·321	neat
m-Cl	−62·72		−9·943	neat
p-Cl	−61·62		−9·957	sat. soln. Et_2O
m-Br	−61·89		−9·860	neat
o-OH	−68·54	−68·5	−9·708	neat
m-OH	−64·89		−9·872	sat. soln. EtOH
p-OH	−65·53		−9·930	sat. soln. EtOH
o-NO_2		−60·0	(−10·37)	sat. soln. $CHCl_3$
m-NO_2		−61·0	(−10·13)	sat. soln. $CHCl_3$
o-CH_3		−64·1	(−10·18)	neat
m-CH_3		−63·6	(−9·90)	neat
p-CH_3		−63·1	(−9·89)	neat
o-OCH_3		−59·7	(−10·39)	neat
m-OCH_3	−63·37		−9·917	neat
p-OCH_3		−62·4	(−9·81)	neat
p-$N(CH_3)_2$		−61·9	(−9·65)	neat

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[5] J. D. Baldeschwieler and E. W. Randall, *Chem. Revs.* **63**, 81 (1963).

[6] W. A. Anderson and R. Freeman, *J. Chem. Phys.* **37**, 85 (1962).

[7] R. E. Klinck and J. B. Stothers, *Canad. J. Chem.* **40**, 1071 (1962).

in Table 1) may be in error slightly since they are for solutions in CCl_4 whereas the carbonyl C^{13} chemical shift measurements of Stothers and Lauterbur were made on neat liquids or saturated solutions.

m-Methoxy and *m*-bromobenzaldehyde were obtained from Light and Co. The other compounds were available elsewhere in this Department. The proton NMR spectra themselves were used as a check for impurities. For the two compounds examined by both the direct and indirect methods, the measured carbonyl C^{13} chemical shifts are within the quoted experimental errors.

DISCUSSION

The effects on chemical shifts as substituents on an aromatic ring are altered have been discussed by several authors. Spiesecke and Schneider[8] have dealt with the H^1 and ring C^{13} chemical shifts in monosubstituted benzenes and Taft[9] has discussed the F^{19} chemical shifts in the mono-substituted fluorobenzenes. On the assumption that both nuclear screening constants and chemical reactivities at the *meta*- and *para*-positions can be related to the local electron charge density, these authors made plots of the chemical shifts against the Hammett σ constants. The Hammett σ functions[10] are experimental parameters measuring the ability of substituents to withdraw or donate charge through a combination of their inductive and resonance effects. Klinck and Stothers,[7] who studied the change in the chemical shift of the formyl proton in substituted benzaldehydes, stated that these changes should be governed by the polarization of the C—H bond. This will be affected by the conjugation between the carbonyl bond and the aromatic ring and hence by substituents on the ring. Stothers and Lauterbur[3] concluded, on the basis of relatively few results, that no correlation appeared to exist between the carbonyl C^{13} chemical shifts in the *meta*- and *para*-substituted benzaldehydes and σ_m or σ_p of the substituents. However, the combined data in Table 1 from their paper and the present work allow this statement to be re-examined.

para-*Substituents*. From the data in Table 1 it can be shown that for the substituted benzaldehydes there is no correlation between the carbonyl C^{13} and the formyl H^1 chemical shifts for either the *meta*- or *para*-series of compounds. Since Klinck and Stothers[7] have shown that the formyl protons in the *para*-substituted benzaldehydes correlate with σ_p, a similar correlation between the carbonyl C^{13} shifts and σ_p in these compounds should not therefore be expected. Figure 1 shows plots of the carbonyl C^{13} shifts in the *meta*- and *para*-substituted benzaldehydes against the σ_m and σ_p values of the substituents respectively. (The crosses with the longer vertical arms represent Lauterbur's measurements, which are of lower accuracy than ours.) The Hammett σ constants used are the revised values of McDaniel and Brown.[11] For the *para*-substituted benzaldehydes no correlation is, in fact, observed between the carbonyl C^{13} shifts and σ_p; no improvement is observed if the separated σ_R parameters are used. The additional results on the *para*-substituted compounds therefore confirm the conclusion of Stothers and Lauterbur.[3] The only significant change in carbonyl C^{13} chemical shift is found for *p*-hydroxybenzaldehyde. The downfield shift here, however, is due to the intermolecular hydrogen bonding of the carbonyl and hydroxyl groups,

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[8] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.* **35**, 731 (1961).

[9] R. W. Taft, *J. Amer. Chem. Soc.* **79**, 1045 (1957).

[10] L. P. Hammett, *Physical Organic Chemistry*. McGraw-Hill New York (1940).

[11] D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958).

which has an electron withdrawing effect on the carbonyl group. An exactly similar effect has been observed on the carbonyl C^{13} shifts in *m*- and *p*-hydroxyacetophenones.[12]

The observations on the substituted benzenes[8] and the mono-substituted fluorobenzenes[9] suggest that the shieldings at the *para*-position arise primarily from changes in the π-electron density brought about by the substituent,[8] and theoretical calculations provide justification for this.[13] Stothers and Lauterbur[3] suggested that the reason why no correlation exists between the carbonyl C^{13} chemical shifts in *para*-substituted benzaldehydes and σ_p, whereas the *para*-H^1 and *para*-C^{13} shifts in the mono-substituted benzenes and the F^{19} shifts in the mono-substituted fluorobenzenes did correlate with σ_p, lies in the fact that the carbonyl carbon atom is not in a comparable position in the resonance system. Resonance forms can be drawn for both electron attracting and electron releasing groups in the *para*-position which suggest that the electron density about the carbonyl carbon nucleus will be little changed. Similar resonance forms indicated that the electron densities of the *para*-H^1 and *para*-C^{13} atoms in the substituted benzenes and the F^{19} atoms in the *para*-substituted fluorobenzenes would be affected by the substituent. Further support for this proposition is found in the observation that the carbonyl C^{13} chemical shifts in the *para*-substituted acetophenones do not correlate with σ_p[12,14] and also from the fact that in the *para*-substituted styrenes, where analogous resonance forms can be drawn, the β-carbon atom C^{13} chemical shifts are affected by the polar characteristics of the substituents whereas the α-carbon atom C^{13} chemical shifts are unaffected.[15] It can be pointed out that the above explanation need not conflict with the fact that the formyl H^1 chemical shifts in the *para*-substituted benzaldehydes correlate with σ_p. Thus, although in the resonance forms the electron density about the carbonyl carbon atom is not altered much, the charge on the oxygen atom does change. The formyl proton could therefore be affected by diamagnetic anisotropy changes as well as by possible changes in the polarization of the C—H bond.

meta-*Substituents.* Figure 1 shows that for *meta*-substituted benzaldehydes a reasonable correlation exists between the carbonyl C^{13} chemical shifts and the σ_m values of the substituents. A plot using the separated σ_I values produces no improvement in linearity. Here, therefore, the additional data have altered the original conclusion of Stothers and Lauterbur.[3] The point for *m*-hydroxybenzaldehyde lies about 1·5 ppm below the best line through the other points but, as stated previously, this is due to intermolecular hydrogen bonding. The changes in carbonyl C^{13} chemical shifts for the *meta*-substituted benzaldehydes therefore appear to be governed mainly by the effect the substituent has upon the conjugation between the aromatic ring and the carbonyl group.

Spiesecke and Schneider[8] have discussed possible effects for the H^1 and C^{13} chemical shifts in the mono-substituted benzenes. These authors commented on the lack of correlation between the *meta*-H^1 and the *meta*-C^{13} chemical shifts in the mono-substituted benzenes with the Hammett σ_m parameters. They recalled that the experimental Hammett σ constants are, in fact, characteristic of di-substituted benzene molecules and their applicability to the *meta*-position in mono-substituted benzenes

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[12] K. S. Dhami and J. B. Stothers, *Canad. J. Chem.* **43**, 479 (1965).

[13] T. K. Wu and B. P. Dailey, *J. Chem. Phys.* **41**, 2796 (1964).

[14] K. S. Dhami and J. B. Stothers, *Tetrahedron Letters* No. 12, 631 (1964).

[15] K. S. Dhami and J. B. Stothers, *Canad. J. Chem.* **43**, 510 (1965).

might be suspect, particularly since the effect of substituents is much smaller at the meta position than at the *para*-position. Wu and Dailey[13] added that when meta di-substituted benzenes were studied some correlations between the changes in chemical shifts and the σ parameters did become apparent, e.g. in the *meta*-substituted fluorobenzenes[9] and in the methyl carbon C^{13} shifts in the *meta*-substituted toluenes.[1] It is interesting to note that the present results show some correlation between the Hammett σ_m parameters and the carbonyl C^{13} shifts in the *meta*-substituted benzaldehydes, which are also di-substituted benzenes, of course. Poor correlation is found between the σ parameters and the formyl proton shifts in the *meta*-substituted benzaldehydes, but Klinck and Stothers[7] suggest that the *meta*-substituents may exert a small effect through space on the formyl proton since these protons with their lack of inner shell electrons, would be more susceptible to anisotropic *meta*-substituents. For the *meta*-substituted acetophenones all the carbonyl C^{13} chemical shifts lie within a very small range and no correlation was observed with σ_m in this case.[12]

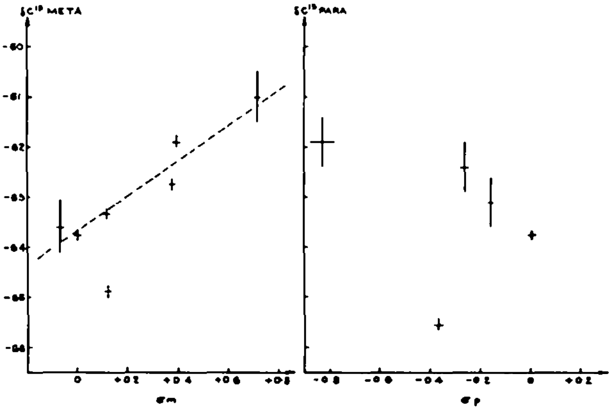

FIG. 1. Plots of the carbonyl C^{13} chemical shifts (in ppm from C_6H_6) for the *meta*- and *para*-substituted benzaldehydes against the Hammett σ_m and σ_p constants respectively

ortho-*Substituents.* A considerable amount of work has been done on the acetyl C^{13} shifts in *ortho*-substituted acetophenones.[3,12,14] Here the dominant effect of the *ortho*-substituents is to cause a downfield shift in both the carbonyl and methyl C^{13} resonances as the size of the substituent increases. This is explained by the steric effect of the *ortho*-substituent which reduces the degree of conjugation between the aromatic ring and the carbonyl groups. Dhami and Stothers[12,14] have shown that, in fact, the carbonyl C^{13} shifts can be used to calculate the angle of twist about the single bond in the conjugated system.

The results in Table 1 for the carbonyl C^{13} shifts in the *ortho*-substituted benzaldehydes show little correlation with the polarity of the substituent. Also the shifts are not in general to lower field relative to benzaldehyde itself or the corresponding *meta*- and *para*-substituted isomers. At first sight this seems to militate against steric hindrance of conjugation being the controlling effect, as in the acetophenone case. However, Fig. 2a shows a plot of the carbonyl C^{13} shifts in the *ortho*-substituted benzaldehydes against the carbonyl C^{13} shifts in the corresponding acetophenones.

The roughly linear relationship between the two sets of carbonyl shifts suggests that the factors controlling both chemical shifts are essentially similar. It is interesting to note that this still applies in the case of the *ortho*-hydroxy substituents. Here the downfield shifts are known to be due primarily to the electron withdrawing effect of the strong intramolecular hydrogen bonding between the carbonyl and hydroxyl groups.

Klinck and Stothers[7] have found that the formyl proton chemical shifts in the *ortho*-substituted benzaldehydes show no correlation with the substituent polarity, but are to lower field than in benzaldehyde and the *meta*- and *para*-isomers (with the one exception of the *o*-hydroxy compound). This was again attributed to steric effects which reduce the conjugative shielding of the ring and hence the polarization of the C—H bond.

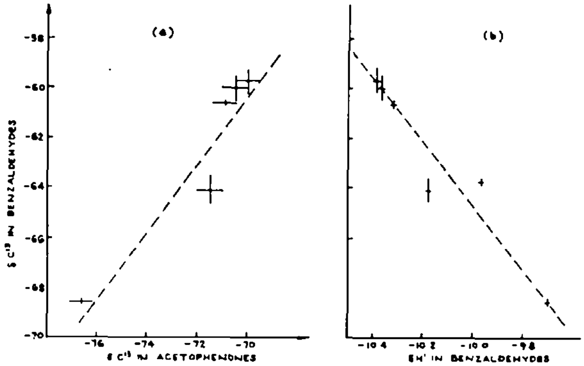

FIG. 2. Plots of the carbonyl C^{13} chemical shifts (in ppm from C_6H_6) for the *ortho*-substituted benzaldehydes against

(a) the carbonyl C^{13} chemical shifts (in ppm from C_6H_6) in the corresponding *ortho*-substituted acetophenones,

(b) the formyl H^1 chemical shifts (in ppm from TMS) in the *ortho*-substituted benzaldehydes.

Figure 2b is a plot of the formyl H^1 shifts against the carbonyl C^{13} shifts for the *ortho*-substituted benzaldehydes. Here it is seen that the formyl H^1 shifts increase roughly linearly as the carbonyl shifts decrease. It appears therefore that there is an overall downfield shift of the formyl protons due to the inhibition of conjugation as the *ortho*-component twists the planes of the aromatic ring and the formyl groups, but that this is opposed by the reduction in the deshielding effect of the aromatic ring current as the formyl proton moves out of the plane of the ring.

It is expected that the absolute values of the carbonyl C^{13} shielding constants will be subject to medium effects. However, in the double resonance experiment the C^{13} chemical shifts are corrected using the H^1 shifts observed at the time of measurement and hence any bulk susceptibility effects will be cancelled out, although a very small differential effect between the protons and the carbonyl carbon atoms may still be present. m- and *p*-Hydroxybenzaldehyde were examined in ethanol and the low carbonyl C^{13} chemical shifts due to hydrogen bonding have already been mentioned. For the two compounds examined in chloroform by the direct method, previous results[3] indicate that a downfield solvent shift of up to 1 ppm for the carbonyl carbon may be present relative to those compounds examined as neat liquids. However, Figs. 1 and 2 show that these possible solvents effects do not affect any of the conclusions drawn from the plots. A discussion of solvent effects on carbonyl C^{13} chemical shifts in general is now available.[16]

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[16] G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.* **42**, 2752 (1965).