Analysis of ^{13}C NMR Spectra of Some Phenyl Acetates

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Summary: Study of ^{13}C chemical shifts, $^{1}J_{^{13}C\text{-}H}$ coupling constants and T_1 measurements lead to reliable analysis of ^{13}C NMR spectra of some phenyl acetates. Influence of some substituents on the electronic environment is reported. The variation of the chemical shifts resulting from different groups allows estimation of the additivity of the chemical shifts of the studied esters. This study confirms the existence of the additive nature of the substituent effect on aryl carbons of the phenyl acetates compared with monosubstituted benzenes.

Introduction

The ^{13}C chemical shifts of aromatic compounds have received considerable attention for the last few years. Aryl carbonyl compounds have gained some interest concerning the substituents effect[1-4].

The present study deals with ^{13}C NMR analysis of mono and di-substituted phenyl acetate and some of their α-choloro acetyl analogous. these investigations are mainly done in order to gain further insight into the factors governing their ^{13}C spectra. There are two major features of the investigation carried out here: One feature was directed to the examination of the additive relationship for the effects of substitutents on aryl and acetoxyl carbons shieldings. The additive properties on aryl carbon shieldings on various benzene derivatives have been already examined[5,6]. According to this data it is possible to predict the shieldings in other derivatives of phenyl acetates. The second feature of the investigation was directed to the effects of substitutents on coupling constants and relaxation times in phenyl acetates.

Experimental

Materials: Monosubstituted benzenes used in this work were obtained from commercial sources. phenyl acetate and other substituted phenolic esters were prepared by standard method; reacting the appropriate phenol with the corresponding acyl chlorides. The observed physical constants of these materials agreed well with the literature values. The structural considerations were confirmed by their proton NMR spectra. NMR Spectra: The ^{13}C spectra of the phenyl acetates were obtained from 1 M $CDCl_3$ solutions on an JEOL JNM-FX 100. The shielding data are given on δ scale relative to tetramethylsilane (0.0δ). Measurements of ^{13}C-H coupling constants and relaxation times were carried out using IRMOD: NOE and inversion recovery methods respectively. Degassed samples have been used for T_1 measurements.

Results and Discussion

The results are summarized in Table I, II, III, and IV. Table I gives the ^{13}C chemical shifts of monosubstituted benzenes in chloroform solution while Table II shows the shielding data of mono-. and disubstituted phenyl acetates. Table III shows the study of α-chloro derivatives of two para-monosubstituted phenyl acetates. The figures for ^{13}C-H coupling and the relaxation times of certain substituted pheyl acetates have been collected in Table IV. The chemical shifts in the Tables were assigned by the aid of known structural effects on ^{13}C shieldings and off-resonance techniques.

The ^{13}C spectrum of phenyl acetate itself shows signal at 169.33 assigned to the carbonyl group. The bridge carbon signal (C-1) arises at 150.77. The C-2 and

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Table I. Chemical shifts for ^{13}C n.m.r. spectra of monosubstituted benzenes.

X		OMe	OAc	Me	Cl	Br	NO_2
$\delta_{(exp)}$	C_1	159.93	150.77	137.71	134.40	122.46	148.43
	Δ	−31.23	−22.07	−9.01	−5.7	+6.24	−19.73
	$C_{2,6}$	114.08	121.53	128.26	128.64	129.87	123.48
	Δ	+14.62	+7.17	+0.44	+0.06	−1.17	5.22
	$C_{3,5}$	129.48	129.37	128.09	129.67	131.38	129.57
	Δ	−0.78	−0.67	+0.61	−0.97	−2.68	−0.87
	C_4	120.66	125.77	125.38	126.41	126.69	134.83
	Δ	+8.04	+2.93	+3.32	+2.29	+2.01	−6.13

Δ) Deviation values of monosubstituted benzenes chemical shifts relative to benzene shift at 128.70.
+Shielding; − deshielding.

C-6 gave one signal at 121.53; while C-3 and C-5 signal appeared at 129.37 and C-4 at 125.77. The upfield signal at 21.05 was assigned to the methyl of the acetyl group. It is apparent from the chemical shifts (Table II) that C-2, C-6, and C-4 are shielded while C-3 and C-5 are slightly deshielded relative to benzene (128.7). The effect is most pronounced at 2-carbons. Shift for C-4 in phenyl acetate[7] is also comparable to that for the corresponding nuclei in anisole[8] and phenol[9]. The assigned shifts may be compared with those predicted by the assumption of additivity of substituents effect at the various aromatic positions[1,3,10,11]. However, it is important to draw attention to the pronounced shielding at ortho and para positions, indicative of electron release to the ring by acetoxyl group canonical structures (b-d).

Since an increase in the electron density is expected at ortho and para positions, the aryl carbons of these positions are considerably shielded in phenyl acetate relative to the value for benzene carbons.

Values for the aryl carbons in phenyl acetates are listed in Table II together with deviations, Δ, from additivity defined as:

$$\Delta = \delta \text{ (calc.)} - \delta \text{ (exp.)}$$

As one might expect, the largest variation of shifts is found in the range 118.8 to 155.1 for the bridge carbon. This large variation reflects the influence of large inductive and resonance effects of the substituents on the electronic environment of the substituted carbon nuclei.

The present data are in good agreement with the expected shielding effects of C-1, C-3 and C-4 by considering the additivity of substituents on 3, and 4- positions in the aryl ring. Table I demonstrates the additivity of chemical shifts in the appropriate monosubstituted benzene. The data for the monosubstituted phenyl acetates in Table II further confirms the existence of the additive nature of substitutent effects on aryl carbon shielding. For the most meta and para substituents, the deviations

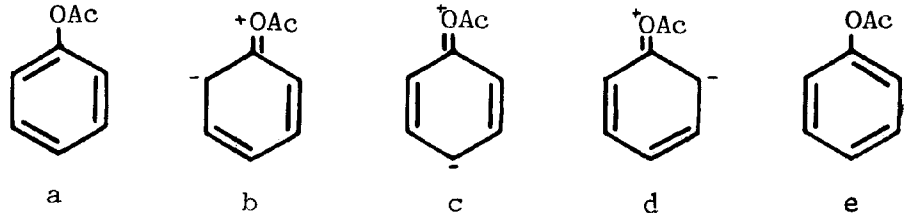
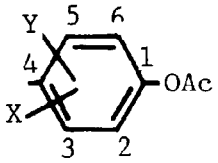


Table II. ^{13}C Chemical shifts in ppm from TMS of some substituted phenyl acetate in (1 M) deuterochloroform.



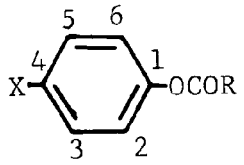
Substituent(s)		Aromatic carbons						Acetyl group carbons	
X	Y	C – 1	C – 2	C – 3	C – 4	C – 5	C – 6	CH_3	C = O
H	H	150.77	121.53	129.37	125.77	(C – 3)	(C – 2)	21.05	169.33
4-CH_3[a]	H	148.48	121.19	129.82	135.32	(C – 3)	(C – 2)	21.00	169.48
Δ		–1.03	–.027	–0.89	–.54			(+0.05)	(–0.68)[d]
4-Cl	H	149.16	122.90	129.42	129.42	(C – 3)	(C – 2)	20.95	169.09
Δ		–0.68	–0.4	–0.11	+2.05			(+0.1)	(+0.21)
4-Br	H	149.76	123.29	132.35	118.80	(C – 3)	(C – 2)	20.95	169.04
Δ		–1.0	+0.92	+1.81	+0.73			(+0.1)	(+0.25)
4-NO_2	H	155.64	122.41	124.14	145.6	(C – 3)	(C – 2)	20.95	168.11
Δ		+1.26	–0.01	–0.99	–0.1			(+0.1)	(+1.19)
3-CH_3[a]	H	150.62	122.12	139.51	126.60	129.09	118.46	21.25	169.58
Δ		–0.46	–1.03	–1.13	–1.27	–0.33	–0.24	(–0.2)	(–0.23)
3-NO_2	H	150.96	117.34	148.77	120.70	130.01	128.10	20.9	168.65
Δ		+0.687	–1.03	+0.33	–0.15	+0.23	–0.44	(+0.15)	(+0.65)
2-CH_3[a]	H	149.35	131.08	126.88	126.08	126.01	121.82	20.71	169.23
Δ		+0.98	–0.54	+2.05	–0.92	+0.06	–0.9	(+0.34)	(+0.07)
2-Cl	H	147.67	130.20	127.67	127.00	127.00	121.20	20.52	168.36
Δ		+3.04	–2.97	+1.64	–0.26	+0.08	+1.3	(+0.53)	(+0.94)
2-NO_3	H	155.1	144.42	124.99	120.22	137.38	119.92	20.76	168.51
Δ		–9.55	–3.16	–0.84	+6.42	–1.88	+2.48	(+0.29)	(–0.79)
3-CH_3[b]	5-CH_3[b]	150.91	119.19	139.12	127.43	139.12	119.19	20.00	169.19
Δ		–1.36	–1.42	–1.35	–2.54	(C – 3)	(C – 2)	(+1.05)	(+0.11)
3-OCH_3[c]	5-OCH_3[c]	151.89	100.48	161.34	98.435	161.34	100.48	21.00	168.92
Δ		+0.44	–1.61	+0.04	–1.91	(C – 3)	(C – 2)	(+0.05)	(+0.38)
2-Cl	3-Cl	148.58	127.58	134.00	127.38	128.31	122.07	20.42	167.83
Δ		+3.1	–0.59	+1.01	–0.7	–0.26	–1.86	(+0.63)	(+1.47)

Δ) Deviation from values calculated from additivity of chemical shifts in the appropriate monosubstituted benzenes (table 1).
a) 2-CH_3 at 16.08 ; 3-CH_3 at 21.05 ; 4-CH_3 at 20.76
b) 3-CH_3 and 5-CH_3 at 21.1
c) 3-OCH_3 and 5-OCH_3 at 55.50
d) Figures in parentheses are deviations from values of parent phenyl acetate.

between the calculated and observed shifts are less than ± 1.27. It is found that only two values deviated larger than 1.27 but less than 2.05. In general, it appears that the combined substituent effects on the aromatic carbon nuclei for the meta and para substituted phenyl acetates are additive to a reasonable approximation.

Introducing chlorine in group R (Table III) showed deviations for aryl carbons compared with aryl carbons in the absence of chlorine atom (Table II). C-2 and C-6 resonance shifted significantly up field compared to C-1 resonance particularly in cresyl derivatives, but C-4 resonance is largely shifted to low field (Table III). This

Table III. ^{13}C Chemical shifts, in ppm from TMS of α-chloro derivatives of cresyl acetate and p-nitrophenyl acetate in 1 M $CDCl_3$.



Compound	Aromatic Carbons				Acetyl Carbons	
	C – 1	C – 2,C – 6	C – 3,C – 5	C – 4	C = O	R
X = CH_3, R = CH_3	148.48	121.91	129.82	135.32	169.48	21.00
X = CH_3, R = CH_2Cl	148.23	120.75	130.01	136.00	165.92	40.84
Δ^a	+0.25	+1.76	–0.19	–0.68	(+3.56)	(–19.84)
X = CH_3, R = $CHCl_2$	148.61	120.73	130.32	136.71	163.47	64.82
Δ	–0.13	+1.18	–0.5	–1.39	(+6.01)	(–43.82)
X = NO_2, R = CH_3	155.64	122.41	125.14	145.6	168.11	20.95
X = NO_2, R = CH_2Cl	154.82	122.17	125.38	145.74	165.20	40.66
Δ^b	+0.84	+0.24	–0.24	–0.14	(+2.91)	(–19.71)
X = NO_2, R = $CHCl_2$	154.47	121.92	125.78	146.10	162.17	63.80
Δ	+1.17	+0.49	–0.64	–0.5	(+5.94)	(–42.85)
X = NO_2, R = CCl_3	154.62	121.62	125.53	146.33	159.59	89.02
Δ	+1.02	+0.79	–0.39	–0.73	(+8.52)	(–68.07)

Δ) deviation from the parent compound; + shielding and – deshielding.
a) The parent for the 4-CH_3 series, Δ considered to be zero.
b) The parent for the 4-NO_2 series, Δ considered to be zero.
Figures in parentheses are deviations, from values as a result of successive replacement of the methyl hydrogen by chlorine atoms.

observation support the delocalization forms.

The observed aryl carbon shieldings differ somewhat from those predicted by assuming additivity of the substituent effects on having one substituent ortho position in phenyl acetate. The additivity is not generally observed, suggesting that steric interference between neighbouring groups upsets their interactions with the ring. Lauterbur[5,6] found several cases in which the usual additivity of substituent effects failed to predict the aryl shielding in orthodisubstituted aromatic systems. In present study, the additivity relation breaks down for C-1 and C-2 in ortho-nitrophenyl acetate producting low field shift for both carbons (Table II); significant shift for C-4 was observed but in the opposite direction. Also, it was found that C-1 shifts to highfield for 2-chloro and 2,3-dichlorophenyl acetates. No appreciable deviation for acyl carbon shieldings was observed in 2-methyl phenyl acetate. We concluded that the C-1 carbons are sensitive to the nature of some ortho substituents (Table II).

In general, the carbonyl carbon showed no remarkable shielding effect as the values vary from 169.48 for 4-methyl substituted to 168.11 for 4-nitro substituted compound. However, these small variations in the shieldings show no correlation with the electronic characteristics of the substituents; the shift for 4-NO_2 derivative is larger than that for its 2-isomer while this observation reversed for 2-chloro and 4-chloro derivatives. The carbonyl carbon shieldings were upfield in comparison to the same carbon in phenyl acetate. Exceptionally, the meta and para methylated derivatives were shifted slightly low field.

Substitution of methyl group hydrogens of acetyl by chlorine led to remarkable upfield shift for the carbonyl carbon, which agreed well with the literature values for carbonyl carbon of α-chloroacetic acid[12] This is interpreted in terms of electronegativity effects. Increasing number of α-chlorine atoms shifts the carboxyl carbon progressively upfield. The electronegativity effects were very clear on shifts of the methyl of acetyl

Table IV. Spin-Lattice Relaxation Times, and Coupling Constant for Some Phenyl Acetate Derivatives.

Compound	C_1	$C_{2,6}$	$C_{3,5}$	C_4	C=O	$-Cx_3$	Others
$C_6H_5OCOCH_3$	58.08[a]	10.9	11.4	7.4	50.5	12.0	–
	–	161.11[b]	162.0	162.4	–	130.6	–
$4\text{-}NO_2C_6H_4OCOCH_3$	52.43	8.31	9.02	55.75	47.34	8.74	–
	–	172.11	173.34	–	–	130.61	–
$4\text{-}NO_2C_6H_4OCOCH_2Cl$	57.47	8.41	8.45	75.82	61.64	8.45	–
	–	166.02	169.68	–	–	152.58	–
$4\text{-}NO_2C_6H_4OCOCHCl_2$	59.04	8.19	8.19	51.20	57.44	10.34	–
	–	167.0	167.0	–	–	181.88	–
$4\text{-}CH_3C_6H_4OCOCH_3$	57.06	7.39	6.22	45.48	49.98	9.06	8.67 $Ph\text{-}CH_3$
	–	162.35	158.69	–	–	129.4	129.4
$3\text{-}CH_3C_6H_4OCOCH_3$	c	7.98 ; 9.36	53.76 ; 5.74	7.65	57.74	9.39	10.21 $Ph\text{-}CH_3$
		163.57 ; 164.8	– ; 158.69	161.13	–	129.40	129.4
$2,3(Cl)_2C_6H_3OCOCHCl_2$	56.01	c ; 3.01	54.49 ; 3.76	4.70	51.01	4.80	–
	–	– ; 167.0	– ; 167.0	167.24	–	180.66	–

a = T_1 in second, b = $1J(^{13}C\text{-}H)$ in Hz, c = not detectable.

group when the hydrogen were substituted by chlorine atoms showing remarkable lowfield shifts (Table III).

The coupling between directly-bonded ^{13}C and $^1H(^1J_{C\text{-}H})$ in the methyl of acetyl group of the acetates was observed to be 130.6 Hz in phenyl acetate (Table IV). This value in typical for sp^3 carbon[13]. When electronegative substituents are introduced to the methyl of the acetyl group, $CH_2Cl(^1J_{C\text{-}H}$ = 152.58 Hz), the coupling increases. Thus electronegativity of chlorine induce a large increase as illustrated above. These results have been compared with aliphatic substituent series CH_4 (125 Hz), CH_3Cl (150 Hz), CH_2Cl_2(178 Hz) and $CHCl_3$(209 Hz)[14,15]. Undoubtedly, the hybridization state of carbon in these compounds is not the same, but changes in the effective nuclear charge on carbon or in the average excitation energy are more likely to be the main source of these variations[16,17], $^1J_{C\text{-}H}$ values of aryl carbons in phenyl acetate series differ slightly from one compound to another due to the different substituents. These substituent effects are largely additive.

We conclude that directly bonded polar substituents appreciably affect the methyl ^{13}C-H coupling constant (Table IV), their influence is markedly attenuated if their effects are transmitted to the methyl group through an aromatic ring. The results for several toluenes, t-butyl benzenes, N,N-dimethyl anilines and anisoles show the relatively small changes observed[18].

Spin-lattice relaxation times(T_1) of ^{13}C nuclei can now be determined in relatively straight forward manner, especially as a result of recent innovations in pulsed FT techniques[19,20]. Generally speaking, spin-lattice relaxation takes place predominantly by dipole-dipole interaction between ^{13}C nucleus and nearby protons, or other neighbouring nuclei such as fluorine[21,22]. TAble IV demonstrates T_1 values for phenyl acetate and some mono and di-substituted phenyl acetates.

T_1 for aryl carbon attached to different groups is as long as expected for quaternary carbons and the values in Table IV are in agreement with some substituted X-group in mono and di-substituted benzenes[23].

Carbonyl carbon T_1 value in phenyl acetate differs somewhat from T_1 of the same carbons in acetophenone (34 sec.) and benzoic acid (35 sec.). A little change of T_1 values of carbonyl may be due to the substituent effect in both α-methyl or in the benzene ring. It is interesting to notice a relationship between signal intensity and the T_1 value in different spectra in this study; the intensity of a ^{13}C signal is inversely proportional to its T_1 value. This was observed for ortho-methyl acetophenone[23]. In principle, directlybonded protons are most effective, and the relative order of T_1 values for carbons bearing three, two, one or no protons should increase. In the absence of other effects the ratio of T_1 values should be 1:2:3 when the number of protons at-

tached to the ^{13}C is three, two or one, respectively[21,22]. This is not the case for phenyl acetates which may indicate further effects such as molecular rotation or tumbling isotropically in solution[24].

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