^{1}H and ^{13}C NMR Spectral Studies on N-(Aryl)-Substituted Acetamides, $C_6H_5NHCOCH_{3-i}X_i$ and 2/4-$XC_6H_4NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and i = 0, 1, 2 or 3)

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35 N-(Phenyl)-, N-(2/4-chlorophenyl)- and N-(2/4-methylphenyl)-substituted acetamides are prepared, characterised and their NMR spectra studied in solution state. The variation of the chemical shifts of the aromatic protons in these compounds follow more or less the same trend with changes in the side chain. The chemical shifts remain almost the same on introduction of Cl substituent to the benzene ring, while that of methyl group lowers the chemical shifts of the aromatic protons. But only ^{13}C-1 and ^{13}C-4 chemical shifts in these compounds are sensitive to variations of the side chain. The incremental shifts in the chemical shifts of the aromatic protons and carbons due to $-COCH_{3-i}X_i$ or $NHCOCH_{3-i}X_i$ groups in all the N-(phenyl)-substituted acetamides, $C_6H_5NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3) are calculated. These incremental chemical shifts are used to calculate the chemical shifts of the aromatic protons and carbons in all the N-(2/4-chlorophenyl)- and N-(2/4-methylphenyl)-substituted acetamides, in two ways. In the first way, the chemical shifts of aromatic protons or carbons are computed by adding the incremental shifts due to $-COCH_{3-i}X_i$ groups and the substituents at the 2nd or 4th position in the benzene ring to the chemical shifts of the corresponding aromatic protons or carbons of the parent aniline. In the second way, the chemical shifts are calculated by adding the incremental shifts due to $-NHCOCH_{3-i}X_i$ groups and the substituents at the 2nd or 4th position in the benzene ring to the chemical shift of a benzene proton or carbon, respectively. Comparison of the two sets of calculated chemical shifts of the aromatic protons or carbons of all the compounds revealed that the two procedures of calculation lead to almost the same values in most cases and agree well with the experimental chemical shifts.

Key words: Nuclear Magnetic Resonance; N-Aryl Substituted Acetamides.

1. Introduction

Amides are of fundamental chemical interest as conjugation between nitrogen lone pair electrons and carbonyl π-bond results in distinct physical and chemical properties [1 – 2]. The amide moiety is a constituent of many biologically important compounds. Many acetanilides exhibit fungicidal, herbicidal and pharmacological activities. Thus we are interested in the spectroscopic and structural aspects of this class of compounds for correlating their activity with the chemical bond parameters.

The ^{35}Cl NQR and infrared spectra of a number of N-(chlorophenyl)-chloroacetamides have been studied [3 – 7]. We have recently prepared several substituted amides of the configuration: $X_yC_6H_{5-y}$-$NHCOCH_{3-y}Cl_y$ (where X = CH_3, NO_2 or Br and $y = 1, 2$ or 3) and measured their ^{35}Cl NQR and IR spectra [6 – 8]. The crystal structures of some of the N-(phenyl)-acetamides have also been determined [9 – 18]. We report herein the NMR spectra of 35 N-(phenyl)- and N-(2/4-chlorophenyl or 2/4-methylphenyl)-substituted acetamides of the constitutions $C_6H_5NHCOCH_{3-i}X_i$ and 2/4-$XC_6H_4NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3) (Table 1).

Table 1. Melting points (°C) of N-(aryl)-substituted acetamides, $ArNHCOCH_{3-i}X_i$.

	2/4-X $C_6H_4NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3)						
Ar	CH_3	CH_2Cl	$CHCl_2$	CCl_3	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$
C_6H_5	114	134	120	83	104	111	134
2-ClC_6H_4	88-90	73	105-107	92	59-60	119	193
4-ClC_6H_4	178	178-180	130-132	63	105	139	128
2-$CH_3C_6H_4$	102	81	130	90	92	116	109
4-$CH_3C_6H_4$	149-151	156	152	104	128	–	102-103

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Table 2. The C=O and N-H infrared absorption frequencies (cm^{-1}) of N-(aryl)-substituted acetamides, $ArNHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

	$CH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3)						
Ar	CH_3	CH_2Cl	$CHCl_2$	CCl_3	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$
	$\gamma_{C=O}$ (str) (cm^{-1})						
C_6H_5	1685.0s	1673.0s	1672.0s	1695.0s	1666.2s	1661.4s	1654.6s
2-Cl C_6H_4	1664.3s	1673.9s	1679.7s	1709.6s	1664.3s	1654.6s	1665.2s
2-CH_3 C_6H_4	1652.7s	1637.0s	1672.0s	1705.0s	1653.7s	1653.7s	1655.6s
4-Cl C_6H_4	–	1670.0s	1681.0s	1709.0s	–	–	–
4-CH_3 C_6H_4	–	1676.0s	1674.0s	1695.0s	–	–	–
	γ_{N-H} (str) (cm^{-1})						
C_6H_5	3305.0s	3266.8s	3269.7s	3290.0s	3258.1s	3299.6s	3312.1s
2-Cl C_6H_4	3241.8s	3266.8s	3254.3s	3299.6s	3288.0s	3242.7s	3369.1s
2-CH_3 C_6H_4	3222.5s	3340.0s	3254.3s	3300.0s	3280.3s	3269.7s	3346.9s
4-Cl C_6H_4	–	3270.0s	3278.0s	3262.0s	–	–	–
4-CH_3 C_6H_4	–	3365.0s	3211.0s	3300.0s	–	–	–

s = strong, m = medium and w = weak.

Table 3. Chemical shifts (δ, ppm) of various aromatic and other protons in N-(phenyl)-substituted acetamides, $C_6H_5NHCOCH_{3-i}$ X_i (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

$COCH_{3-i}$ X_i	δ, ppm				
	H-2,6	H-3,5	H-4	N-H	Alkyl H
$COCH_3$	7.50d	7.20t	7.02t	8.94	2.05
$COCH_2Cl$	7.47d	7.27t	7.10t	8.33	4.00
$COCHCl_2$	7.52d	7.32t	7.17t	8.53	6.11
$COCCl_3$	7.53d	7.33t	7.18t	8.48	–
$COCH_2CH_3$	7.60d	7.22t	6.97	9.57	2.35, 1.15
$COCH(CH_3)_2$	7.57d	7.26t	7.06t	7.97	2.52, 1.20
$COC(CH_3)_3$	7.49d	7.22t	7.01t	7.76	1.25
H	6.48	7.05	6.67	3.39	–

Table 4. The incremental shifts in chemical shifts (δ, ppm) of aromatic protons due to -$COCH_{3-i}X_i$ and -$NHCOCH_{3-i}X_i$ groups in N-(phenyl)-substituted acetamides, $C_6H_5NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

$COCH_{3-i}X_i$	H-2,6	H-3,5	H-4	$NHCOCH_{3-i}X_i$	H-2,6	H-3,5	H-4
$COCH_3$	1.02	0.15	0.35	$NHCOCH_3$	0.40	−0.2	−0.30
$COCH_2Cl$	0.99	0.22	0.43	$NHCOCH_2Cl$	0.20	0.0	−0.17
$COCHCl_2$	1.04	0.27	0.50	$NHCOCHCl_2$	0.25	0.05	−0.10
$COCCl_3$	1.05	0.28	0.51	$NHCOCCl_3$	0.26	0.06	−0.06
$COCH_2CH_3$	1.12	0.17	0.30	$NHCOCH_2CH_3$	0.33	−0.17	−0.31
$COCH(CH_3)_2$	1.09	0.21	0.39	$NHCOCH(CH_3)_2$	0.27	−0.01	−0.21
$COC(CH_3)_3$	1.01	0.17	0.34	$NHCOC(CH_3)_3$	0.22	−0.05	−0.26

2. Experimental

Materials and Methods: The N-(phenyl)-, N-(2-chlorophenyl)-, N-(2-methylphenyl)-, N-(4-chlorophenyl)- and N-(4-methylphenyl)- substituted acetamides (Table 1) were prepared from substituted anilines, substituted acetic acids (Aldrich, Germany) and thionyl chloride [18–21]. The commercial anilines (Sisco Research Laboratories, India) were purified by either double distillation or zone refining. All other reagents employed in the preparations and purification of reagents were of analytical grade. Pure samples of the respective anilines (aniline, 2-chloroaniline, 2-methylaniline, 4-chloroaniline or 4-methylaniline) were treated with mixtures of respective acetic acids (acetic acid, 2-chloroacetic acid, 2,2-dichloroacetic acid, 2,2,2-trichloroacetic acid, 2-methylacetic acid, 2,2-dimethylacetic acid or 2,2,2-trimethylacetic acid) and thionyl chloride with constant stirring. The resulting mixtures were slowly warmed to expel HCl. Excess thionyl chloride was hydrolysed by adding cold water dropwise under ice cold conditions. HCl produced was removed by treating with excess 2M NaOH. The solids separated were filtered under suction, washed thoroughly with water and dried. The N-(aryl)-substituted acetamides thus prepared were recrystallised from ethanol several times to the constant melting points (Table 1). The compounds have been further characterised by recording their infrared spectra (Table 2) [21].

Table 5. Shifts in the position of benzene protons (δ, 7.27) caused by the substituents.

Substituent	ortho	meta	para
-CH_3, -R	−0.15	−0.10	−0.10
-COOH, -COOR	+0.80	+0.15	+0.20
-CN	+0.30	+0.30	+0.30
-$CONH_2$	+0.50	+0.20	+0.20
-COR	+0.60	+0.30	+0.30
-SR	+0.10	−0.10	−0.20
-NH_2, -NHR	−0.80	−0.15	−0.40
-$N(CH_3)_2$	−0.50	−0.20	−0.50
-I	+0.30	−0.20	−0.10
-CHO	+0.70	+0.20	+0.40
-Br	0.00	0.00	0.00
-NHCOR	+0.40	−0.20	−0.30
-Cl	0.00	0.00	0.00
-F	+0.30	+0.02	+0.22
-NH_3^+	+0.40	+0.20	+0.20
-OR	−0.20	−0.20	−0.20
-OH	−0.40	−0.40	−0.40
-OCOR	+0.20	−0.10	−0.20
-NO_2	+1.00	+0.30	+0.40
-SO_3H, -SO_2NH_2	+0.40	+0.10	+0.10

2.1. NMR Spectral Measurements

The proton and carbon-13 NMR spectra of the compounds were measured on a BRUKER Ac 300F, 300 MHz FT-NMR spectrometer. The spectra were recorded in $CDCl_3$ and DMSO with tetramethylsilane (Me_4Si) as internal standard. The experimental conditions employed for ^{1}H NMR spectra were as follows.

Table 6. Chemical shifts (δ, ppm) of various aromatic and other protons in N-(2-chlorophenyl)-substituted acetamides, 2-$ClC_6H_4NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

$COCH_{3-i}X_i$	H-3			H-4			H-5			H-6			N-H	Alkyl H
	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	obs.
$COCH_3$	7.3d	7.20	7.20	7.16t	7.02	7.02	7.17d	7.20	7.20	8.10d	6.83	7.50	7.76	2.2
$COCH_2Cl$	7.25d	7.27	7.27	7.05t	7.10	7.07	7.25t	7.27	7.25	8.30d	7.47	7.47	8.89	4.20
$COCHCl_2$	7.24d	7.32	7.32	7.06t	7.17	7.17	7.35t	7.32	7.32	8.20d	7.52	7.52	8.72	6.09
$COCCl_3$	7.26d	7.33	7.33	7.08t	7.18	7.18	7.35t	7.33	7.33	8.17d	7.53	7.53	8.98	–
$COCH_2CH_3$	7.3d	7.22	7.22	6.98t	6.97	6.97	7.20t	7.22	7.22	8.28d	7.60	7.60	7.78	2.23, 1.23
$COCH(CH_3)_2$	7.33d	7.26	7.26	7.0t	7.06	7.06	7.23t	7.26	7.26	8.35d	7.57	7.57	7.74	2.59, 1.27
$COC(CH_3)_3$	7.29d	7.22	7.26	6.96t	7.01	7.01	7.20t	7.22	7.26	8.35d	7.49	7.79	8.0	1.52, 1.31, 1.10
H	7.13		–	6.93		–	7.13		–	6.59		–	3.85	–

Table 7. Chemical shifts (δ, ppm) of various aromatic and other protons in N-(2-methylphenyl)-substituted acetamides, 2-$CH_3C_6H_4NHCOCH_{3-i}X_i$ (X = Cl or CH_3, and $i = 0$, 1, 2 or 3).

$COCH_{3-i}X_i$	H-3			H-4			H-5			H-6			N-H	Alkyl H
	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	obs.
$COCH_3$	7.22d	7.05	7.05	7.10t	6.92	6.92	7.00t	7.10	7.10	7.54d	7.40	7.40	7.62	2.16, 1.90
$COCH_2Cl$	7.17d	7.12	7.12	7.08t	7.00	7.00	7.17t	7.17	7.17	7.74d	7.37	7.37	8.26	4.13, 2.22
$COCHCl_2$	7.13d	7.17	7.17	7.13t	7.07	7.07	7.21t	7.22	7.22	7.68d	7.42	7.42	8.14	6.05, 2.26
$COCCl_3$	7.18d	7.18	7.18	7.11t	7.08	7.11	7.37t	7.23	7.23	7.61d	7.43	7.43	8.28	2.40, 2.24
$COCH_2CH_3$	7.11d	7.07	7.07	7.02t	6.87	6.87	7.11t	7.12	7.12	7.57d	7.50	7.50	7.48	2.32, 2.16, 1.17
$COCH(CH_3)_2$	7.10d	7.11	7.11	7.02t	6.96	6.96	7.10t	7.16	7.16	7.58d	7.47	7.47	7.47	2.52, 2.15, 1.16
$COC(CH_3)_3$	7.19d	7.05	7.07	7.04t	6.91	6.91	7.16t	7.12	7.12	7.75d	7.39	7.69	7.31	2.21, 1.30
H	6.97		–	6.64		–	6.97		–	6.49		–	3.31	2.01

Table 8. Chemical shifts (δ, ppm) of various aromatic and other protons in N-(4-chlorophenyl)-substituted acetamides, 4-$ClC_6H_4NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

$COCH_{3-i}X_i$	H-2,6			H-3,5			N-H	Alkyl H
	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	obs.
$COCH_3$	7.58d	6.83	7.50	7.22d	7.20	7.25	9.61	2.06
$COCH_2Cl$	7.47d	7.47	7.47	7.22d	7.27	7.27	7.76	4.00
$COCHCl_2$	7.47d	7.52	7.52	7.32t	7.32	7.32	8.09	6.02
$COCCl_3$	7.45d	7.53	7.53	7.28d	7.33	7.33	8.44	–
$COCH_2CH_3$	7.41d	7.60	7.60	7.18d	7.22	7.22	8.11	2.33, 1.18
$COCH(CH_3)_2$	7.41d	7.57	7.57	7.18d	7.26	7.26	7.75	3.42, 1.16
$COC(CH_3)_3$	7.46d	7.49	7.79	7.22d	7.22	7.26	7.56	1.27
H	6.48		–	7.03		–	3.59	–

Table 9. Chemical shifts (δ, ppm) of various aromatic and other protons in N-(4-methylphenyl)-substituted acetamides, 4-$CH_3C_6H_4NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

$COCH_{3-i}X_i$	H-2,6			H-3,5			N-H	Alkyl H
	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	obs.
$COCH_3$	7.39d	6.38	7.47	7.06d	6.90	7.05	8.18	2.10, 2.26
$COCH_2Cl$	6.19d	7.37	7.37	6.19d	7.12	7.12	8.35	2.13, 2.85
$COCHCl_2$	7.47d	7.42	7.52	7.11d	7.17	7.32	8.91	2.29, 6.33
$COCCl_3$	7.40d	7.43	7.43	7.15d	7.18	7.18	8.44	2.31
$COCH_2CH_3$	7.37d	7.70	7.50	6.97d	7.07	7.17	8.30	2.27, 1.15
$COCH(CH_3)_2$	7.37d	7.57	7.47	6.97d	7.26	7.16	8.30	2.25, 1.16
$COC(CH_3)_3$	7.40d	7.47	7.69	7.05d	7.11	7.16	7.51	2.27, 1.26
H	6.49		–	6.89		–	3.59	2.18

The spectral frequency (SF) was kept at 300.134 MHz, sweep width (SW) at 6024.096, pulse width (PW) at 8.0, relaxation delay (RD) of 1.0 (sec), acquisition time (AQ) was 1.360 (sec), receiver gain (RG) 10, decoupling power (DP) was 63L CPD, filter to suppress noise (LB) 0.0, reference value (SR) was set at 4125.36 ppm for H_2O internally. For ^{13}C NMR spectra, the spectral frequency (SF) was kept at 75.469 MHz, sweep width (SW) at 22727.273, pulse width (PW) at 5.0, relaxation delay (RD) of 1.0 (sec), acquisition time (AQ) was 0.360 (sec), receiver gain (RG) 400, decoupling power (DP) was 14H CPD, filter to suppress noise (LB) 6.0, reference value (SR) was set at 701.89 ppm for DMSO at 39.5 ppm externally.

3. Results and Discussion

3.1. ^{1}H NMR Spectra

The ^{1}H chemical shift values of N-(phenyl)-substituted acetamides are shown in Table 3. Since the chemical shift depends on the electron density around the nucleus or associated with the atom to which it is bonded, the incremental shifts of the aromatic protons (ppm) due to $-COCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2, 3) in all the N-(phenyl)-substituted acetamides, $C_6H_5NHCOCH_{3-i}X_i$ were calculated by comparing the proton chemical shifts of these compounds with those of aniline proton values of H-2,6 =

Table 10. Chemical shifts (δ, ppm) of various aromatic and other carbons in N-(phenyl)-substituted acetamides, $C_6H_5NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

-$COCH_{3-i}$ X_i	δ, ppm					
	C-1	C-2,6	C-3,5	C-4	C=O	Alkyl C
$COCH_3$	138.1	120.4	128.5	124.0	169.3	23.8
$COCH_2Cl$	136.8	120.4	128.9	125.1	164.2	42.9
$COCHCl_2$	136.2	120.6	129.2	125.8	162.3	66.9
$COCCl_3$	135.9	120.6	129.1	126.0	159.3	92.9
$COCH_2CH_3$	139.0	119.3	128.7	122.8	172.2	29.7, 9.5
$COCH(CH_3)_2$	138.2	120.0	128.8	124.0	175.9	36.4, 19.6
$COC(CH_3)_3$	138.1	120.4	128.3	123.7	176.6	39.2, 27.2
H	146.2	114.6	128.8	117.8	–	–

Table 11. The incremental shifts in chemical shifts of aromatic carbons due to -$COCH_{3-i}X_i$ and -$NHCOCH_{3-i}X_i$ groups in N-(phenyl)-substituted acetamides, $C_6H_5NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

-$COCH_{3-i}X_i$	C-1	C-2,6	C-3,5	C-4	$NHCOCH_{3-i}X_i$	C-1	C-2,6	C-3,5	C-4
$COCH_3$	−8.1	5.8	−0.3	6.2	$NHCOCH_3$	9.6	−8.1	0.0	−3.4
$COCH_2Cl$	−9.4	5.8	−0.1	7.3	$NHCOCH_2Cl$	8.3	−8.1	0.4	−4.5
$COCHCl_2$	−10.0	6.0	0.4	8.0	$NHCOCHCl_2$	8.4	−7.9	0.7	−2.7
$COCCl_3$	−10.3	6.0	0.3	8.2	$NHCOCCl_3$	7.4	−7.9	0.6	−2.5
$COCH_2CH_3$	−7.2	4.7	−0.1	5.0	$NHCOCH_2CH_3$	10.5	−9.2	0.1	−6.0
$COCH(CH_3)_2$	−8.0	5.4	0.0	6.2	$NHCOCH(CH_3)_2$	9.7	−8.4	0.3	−4.4
$COC(CH_3)_3$	−8.1	5.8	−0.5	5.9	$NHCOC(CH_3)_3$	9.7	−8.0	−0.2	−4.8

6.48 ppm, H-3,5 = 7.05 ppm, H-4 = 6.67 ppm. The calculated values are shown in Table 4. Similarly the incremental shifts of the aromatic protons (ppm) in N-phenyl substituted acetamides due to –$NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2, 3) were calculated by comparing the proton chemical shifts of these compounds with those of benzene proton value of 7.27 ppm. The calculated values are also shown in Table 4.

Then the chemical shifts of all the aromatic protons in all the N-(2/4-chlorophenyl)- and N-(2/4-methylphenyl)-substituted acetamides, 2/4-XC_6H_4NHCO-$CH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3) were calculated in two ways by adding substituent contributions to the chemical shifts of either aniline protons or benzene proton, as per the principle of substituent addition. In the first method, the chemical shifts of various aromatic protons in these compounds were computed by adding the shifts due to –$COCH_{3-i}X_i$ groups (Table 4) and the shifts due to the substituents (Table 5) [22–24] at the 2nd or 4th position in the benzene ring to the chemical shifts of the corresponding aromatic protons of the parent aniline. In the second method, the chemical shifts of various aromatic protons of N-(2/4-chlorophenyl)- and N-(2/4-methylphenyl)-substituted acetamides were calculated by adding the shifts due to –$NHCOCH_{3-i}X_i$ groups (Table 4) and the substituents (Table 5) at the 2nd or 4th position in the benzene ring to the chemical shift of benzene proton.

Table 12. Incremental shifts of the aromatic atoms of mono-substituted benzenes (ppm from benzene at 128.5 ppm, +downfield, −upfield) carbon atom of substituents from TMS.

Substituent	C-1	C-2 (Attachment)	C-3	C-4	C of substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	–
CH_3	+9.3	+0.7	−0.1	−2.9	21.3
CH_2CH_3	+15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
C_6H_5	+12.1	−1.8	−0.1	−1.6	–
OH	+26.6	−12.7	+1.6	−7.3	
OCH_3	+31.4	−14.4	+1.0	−7.7	54.1
COOH	+2.9	+1.3	+0.4	+4.3	168.0
NH_2	+19.2	−12.4	+1.3	−9.5	–
NO_2	+19.6	−5.3	+0.9	+6.0	–
F	+35.1	−14.3	+0.9	−4.5	–
Cl	+6.4	+0.2	+1.0	−2.0	–
Br	−5.4	+3.4	+2.2	−1.0	–
I	−32.2	+9.9	+2.6	−7.3	–
SO_2NH_2	+15.3	−2.9	+0.4	+3.3	–

These calculated chemical shifts of different aromatic protons of N-(2/4-chlorophenyl)- and N-(2/4-methylphenyl)-substituted acetamides are shown in Tables 6–9.

3.2. ^{13}C NMR Spectra

The ^{13}C chemical shifts of N-(phenyl)-substituted acetamides, $C_6H_5NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3) are shown in Table 10. The incremental shifts of the aromatic carbons (ppm) due to –$COCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3) in all the N-(phenyl) substituted acetamides were calculated by comparing the chemical shifts of aromatic carbons of these compounds with those of aniline carbon values of C-1 = 146.2 ppm, C-2,6 = 114.6 ppm, C-3,5 = 128.8 ppm, C-4 = 117.8 ppm. Similarly the incremental shifts of the aromatic carbons (ppm) due to –$NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3) in N-phenyl substituted acetamides were also calculated, by comparing the chemical shifts of aromatic carbons of these compounds with the benzene carbon value of 128.5 ppm. The calculated values are shown in Table 11. These values were used to calculate the chemical shifts of all the aromatic carbons in all the N-

Table 13. Chemical shifts (δ, ppm) of various aromatic and other carbons in N-(2-chlorophenyl)-substituted acetamides, 2-ClC_6H_4NHCO$CH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

	δ, ppm																			
$COCH_{3-i}X_i$	C-1			C-2			C-3			C-4			C-5			C-6			C=0	Alkyl C
	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	obs.
$COCH_3$	133.5	137.8	138.3	127.7	126.8	126.9	129.2	128.7	128.7	123.6	125.0	125.0	128.6	126.8	126.5	122.9	121.4	121.4	162.2	24.4
$COCH_2Cl$	133.5	137.0	137.0	127.6	126.8	126.8	129.0	128.9	129.1	125.3	126.1	126.0	127.6	126.7	126.9	121.1	121.4	121.4	163.8	43.0
$COCHCl_2$	133.1	136.4	136.9	127.3	127.0	127.0	129.2	129.4	129.4	127.7	126.8	126.8	127.7	127.2	127.2	121.6	121.6	122.1	161.5	66.9
$COCCl_3$	132.5	136.1	136.1	126.2	127.0	127.0	129.0	129.3	129.3	126.2	127.0	127.0	127.6	127.1	127.1	121.2	121.6	121.6	158.6	92.0
$COCH_2CH_3$	134.4	139.2	139.2	124.3	125.7	125.7	128.7	128.9	128.7	122.8	123.8	123.5	127.3	126.7	126.6	121.6	120.3	121.4	171.9	30.6, 9.4
$COCH(CH_3)_2$	134.6	138.4	138.4	124.4	126.4	126.5	128.8	129.0	129.0	122.7	125.0	125.0	127.5	126.0	126.8	121.6	121.0	120.3	175.1	36.8, 19.5
$COC(CH_3)_3$	134.5	138.3	138.3	124.1	126.8	126.8	128.5	128.5	128.5	122.7	124.7	124.7	127.5	126.3	126.3	121.3	121.4	121.4	176.2	39.8,27.2
H	142.7	–	–	118.6	–	–	129.0	–	–	118.6	–	–	127.4	–	–	115.7	–	–	–	–

Table 14. Chemical shifts (δ, ppm) of various aromatic and other carbons in N-(2-methylphenyl)-substituted acetamides, 2-$CH_3C_6H_4$NHCO$CH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

	δ, ppm																			
$COCH_{3-i}X_i$	C-1			C-2,6			C-3,5			C-4			C-5			C-6			C=0	Alkyl C
	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	obs.
$COCH_3$	135.5	138.3	140.3	126.3	129.7	127.9	130.4	129.2	129.4	124.2	123.9	122.8	125.5	125.6	125.8	124.2	120.3	118.5	168.9	23.8, 17.7
$COCH_2Cl$	134.6	137.5	136.8	130.4	129.7	129.7	129.5	129.4	129.5	125.7	125.0	125.0	126.6	125.8	126.0	122.7	120.3	120.3	164.0	43.0, 17.4
$COCHCl_2$	133.9	136.9	136.9	130.7	129.9	129.9	130.2	129.9	129.9	126.5	125.7	125.7	126.9	126.3	126.3	123.2	120.5	120.5	162.2	67.0, 17.4
$COCCl_3$	133.9	136.6	136.6	131.2	129.9	129.9	130.7	129.8	129.8	123.4	125.9	125.9	126.8	126.2	126.2	121.7	120.5	120.5	159.4	93.1, 17.5
$COCH_2CH_3$	135.7	139.7	139.7	126.3	128.6	128.6	130.3	129.4	129.3	123.9	122.7	123.9	125.2	125.8	125.7	123.9	119.2	119.2	172.5	30.1, 17.7, 9.8
$COCH(CH_3)_2$	135.7	138.9	138.9	126.3	129.3	129.4	130.3	129.5	129.5	123.9	123.9	123.7	125.2	125.9	125.4	123.9	119.9	120.3	175.5	36.0, 19.6, 17.6
$COC(CH_3)_3$	135.8	138.8	138.9	126.6	129.7	129.7	130.3	129.0	129.0	123.2	123.6	123.7	125.0	125.4	125.4	123.2	120.3	120.4	176.5	39.6, 27.6, 17.6
H	144.3		–	124.6		–	129.7		–	117.7		–	126.2		–	114.3		–	–	16.4

Table 15. Chemical shifts (δ, ppm) of various aromatic and other carbons in N-(4-chlorophenyl)-substituted acetamides, 4-ClC_6H_4NHCO$CH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

	δ, ppm													
$COCH_{3-i}X_i$	C-1			C-2,6			C-3,5			C-4			C=0	Alkyl C
	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	obs.
$COCH_3$	137.6	136.1	136.1	120.4	121.4	121.4	127.0	128.7	129.2	128.0	130.4	130.4	168.3	23.68
$COCH_2Cl$	134.6	134.8	134.8	121.6	121.4	121.4	129.5	128.9	129.1	130.4	131.5	131.5	163.0	40.02
$COCHCl_2$	135.0	134.2	134.2	121.6	121.6	121.6	129.4	129.4	129.4	131.2	132.2	132.2	161.9	66.93
$COCCl_3$	134.5	133.9	133.9	122.1	121.6	121.6	129.2	129.3	129.3	131.5	132.4	132.4	159.5	92.75
$COCH_2CH_3$	136.7	137.0	137.0	121.6	120.3	120.3	128.7	128.9	128.8	129.0	129.2	128.9	172.7	30.40, 9.51
$COCH(CH_3)_2$	136.7	136.2	136.2	121.5	121.0	121.1	128.7	129.0	129.0	129.0	130.4	130.5	175.1	36.40, 19.41
$COC(CH_3)_3$	136.6	138.1	136.1	121.6	120.4	121.5	128.7	128.3	128.5	129.0	130.1	130.2	178.0	39.59, 27.51
H	144.9		–	116.1		–	128.9		–	122.6		–	–	–

Table 16. Chemical shifts (δ, ppm) of various aromatic and other carbons in N-(4-methylphenyl)-substituted acetamides, 4-$CH_3C_6H_4$NHCO$CH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

	δ, ppm													
$COCH_{3-i}X_i$	C-1			C-2,6			C-3,5			C-4			C=0	Alkyl C
	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	calc.1	calc.2	obs.	obs.
$COCH_3$	135.5	135.2	135.2	120.3	120.3	121.1	129.3	129.2	129.2	133.8	133.3	133.2	169.0	24.3, 20.8
$COCH_2Cl$	133.2	133.9	133.9	119.7	120.3	120.3	128.7	129.4	129.6	135.0	134.4	134.4	164.1	42.9, 20.2
$COCHCl_2$	134.1	133.3	133.3	119.1	120.5	120.5	129.0	129.9	129.9	134.3	135.1	135.1	161.1	66.8, 20.5
$COCCl_3$	133.3	133.0	133.0	120.6	120.5	121.3	129.7	129.8	129.0	135.8	135.3	135.3	159.3	92.7, 20.9
$COCH_2CH_3$	135.7	136.1	136.1	120.5	119.2	120.0	129.1	129.4	128.5	130.6	132.1	131.8	172.7	30.4, 9.5
$COCH(CH_3)_2$	135.5	135.3	135.3	120.2	119.9	120.8	129.0	129.5	128.7	133.5	133.3	133.3	175.1	36.0, 19.6, 17.6
$COC(CH_3)_3$	135.5	135.2	135.3	120.3	120.4	121.2	129.1	129.0	128.2	133.5	132.9	133.0	176.5	39.4, 27.5, 20.7
H	143.8		–	115.0		–	129.5		–	127.2		–	–	20.2

(2/4-chlorophenyl)- and N-(2/4-methylphenyl)- substituted acetamides, 2/4-XC_6H_4NHCO$CH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3) in two ways by adding substituent contributions (Table 12) [22–24] to the chemical shifts of either aniline carbons or benzene carbons, as described under ^{1}H NMR spectra. The calculated chemical shifts of different aromatic carbons in all the N-(2/4-chlorophenyl)- and N-(2/4-methylphenyl)-substituted acetamides are shown in Tables 13–16.

4. Comparisons and Conclusions

Comparison of the two sets of calculated chemical shifts of the aromatic protons and carbons in N-(2/4-chlorophenyl)- and N-(2/4-methylphenyl)-substituted acetamides revealed that the two procedures of calculation lead to almost the same values in most cases, which agree well with the experimental chemical shifts. This has indicated that the principle of additivity of the substituent effects is valid in these compounds.

[1] The Chemistry of Amides, ed., J. Jabicky; Interscience, London 1970.
[2] S. R. Sandler and W. Karo, Organic Functional Group Preparations; Academic Press, London 1972, Vol. 3.
[3] W. Pies, H. Rager, and Al. Weiss, Org. Mag. Reson. **3**, 147 (1971).
[4] B. T. Gowda and Al. Weiss, Z. Naturforsch. **49a**, 695 (1994).
[5] B. T. Gowda, D. K. Bhat, H. Fuess, and Al. Weiss, Z. Naturforsch. **54a**, 261, 679 (1999).
[6] B. T. Gowda, B. H. A. Kumar, and H. Fuess, Z. Naturforsch. **55a,** 721 (2000).
[7] D. K. Bhat and B. T. Gowda, J. Indian Chem. Soc. **77**, 279 (2000).
[8] B. H. A. Kumar and B. T. Gowda, J. Indian Chem. Soc. **79**, 163 (2002)
[9] S. Kashino, K. Ito, and M. Haisa, Bull. Chem. Soc. Japan **52**, 365 (1979).
[10] V. Nagarajan, H. Paulus, N. Weiden, and Al. Weiss, J. Chem. Soc. Faraday Trans. 82, 1499 (1986).
[11] D. Groke, S. Dou, and Al. Weiss, Z. Naturforsch. **47a,** 160 (1992).
[12] S. Dou, B. T. Gowda, H. Paulus, and Al. Weiss, Z. Naturforsch. **49a**, 1136 (1994).
[13] B. T. Gowda, S. Dou, and Al. Weiss, Z. Naturforsch. **51a**, 627 (1996).
[14] S. Dou, H. Fuess, Al. Weiss, B. T. Gowda, and V. G. Krishnan, Z. Kristallogr. **212**, 532 (1997).
[15] B. T. Gowda, I. Svoboda, and H. Fuess, Z. Naturforsch. **55a**, 779 (2000).
[16] B. T. Gowda, H. Paulus, and H. Fuess, Z. Naturforsch. **55a**, 791 (2000).
[17] B. T. Gowda, H. Paulus, and H. Fuess, Z. Naturforsch. **56a**, 386 (2001).
[18] B. T. Gowda, K. Jyothi, H. Paulus, and H. Fuess, Z. Naturforsch. **58a**, 225 (2003).
[19] W. A. Jacobs and M. Heidelberger, J. Biol. Chem. **21**, 104 (1915).
[20] A. J. Hill and E. B. Kelsey, J. Amer. Chem. Soc. **44**, 2357 (1922).
[21] B. T. Gowda, K. Jyothi, and N. Damodara, J. Indian Chem. Soc. **80** (2003), to be published.
[22] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, Spectrometric Identification of Organic Compounds; John Wiley and Sons, New York 1991.
[23] W. Kemp, Organic Spectroscopy; MacMillan, London 1996.
[24] D. E. Ewing, Org. Magn. Reson. **12**, 499 (1979).