^{1}H and ^{13}C NMR Spectral Studies on *N*-(*j*,*k*-Dichlorophenyl)- and *N*-(*j*,*k*-Dimethylphenyl)-acetamides and Substituted Acetamides

Shilpa and Basavalinganadoddy Thimme Gowda

Department of Post-Graduate Studies and Research in Chemistry, Mangalore University, Mangalagangothri-574 199, Mangalore, India

Reprint requests to Prof. B. T. G.; E-mail: gowdabt@yahoo.com

Z. Naturforsch. **62a,** 84 – 90 (2007); received October 16, 2006

70 *N*-(*j*,*k*-Dichlorophenyl / *j*,*k*-dimethylphenyl)-acetamides and substituted acetamides of the general formula *j*,*k*-$X'_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (*j*,*k* = 2,3; 2,4; 2,5; 3,4 or 3,5; X, X′ = Cl or CH_3; *i* = 0, 1, 2 or 3) have been synthesized and their ^{1}H and ^{13}C NMR spectra in solution were studied. The influence of Cl and methyl substitution in the side chain as well as in the aryl group was systematically investigated and discussed in detail. Chemical shifts of all aromatic protons and carbon atoms were computed by adding the substituent contributions in three different ways to those of the unsubstituted molecules. The agreement with the experimental values is discussed in detail for the three different methods of calculation.

Key words: ^{1}H/^{13}C NMR; *N*-(Dichlorophenyl/Dimethylphenyl)-acetamides/Substituted Acetamides.

1. Introduction

The amide moiety is an important constituent of many biologically significant compounds. Hence an understanding of the formation, properties and reactions of amides is central for future development in such areas like polypeptide and protein chemistry. Many amides exhibit fungicidal, herbicidal and pharmacological activities. Thus we are interested in the synthetic, spectroscopic and structural aspects of this class of compounds [1 – 5]. We have recently reported on synthetic, infrared and NMR spectral studies of several *N*-(aryl)-acetamides and substituted acetamides [3 – 5]. In continuation of these efforts of correlating spectroscopic parameters with the chemical bond parameters, 70 *N*-(*j*,*k*-dichlorophenyl/*j*,*k*-dimethylphenyl)-acetamides and substituted acetamides of the general formula *j*,*k*-$X'_2C_6H_3NH$-CO-$CH_{3-i}X_i$ where *j*,*k* = 2,3; 2,4; 2,5; 3,4 or 3,5; X, X′ = Cl or CH_3; *i* = 0, 1, 2 or 3 have been synthesized and their ^{1}H and ^{13}C NMR spectra were measured in solution and correlated.

2. Experimental

2.1. Materials and Methods

The 70 substances mentioned in Table 1 were prepared from *j*,*k*-dichloroanilines / *j*,*k*-dimethylanilines (*j*,*k*-$X_2C_6H_3NH_2$, where *j*,*k* = 2,3; 2,4; 2,5; 3,4 or 3,5; X = Cl or CH_3), substituted acetic acids ($CH_{3-i}X_iCOOH$, where X = Cl or CH_3; *i* = 0, 1, 2 or 3) and thionyl chloride [1, 3 – 8].

The commercially available anilines (Aldrich, Germany) 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 were treated with mixtures of respective acetic acid (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 under constant stirring. The resulting mixtures were slowly warmed to expel HCl. Excess thionyl chloride was hydrolyzed by adding cold water dropwise under ice-cold conditions. The HCl produced was removed by treating with excess 2 M NaOH. The separated solids were filtered under suction, washed thoroughly with water and dried. All the 70 *N*-(*j*,*k*-dichlorophenyl)- and *N*-(*j*,*k*-dimethylphenyl)-acetamides and substituted acetamides (Table 1) thus prepared were recrystallized from ethanol several times to constant melting points. The purity of the compounds was further checked by recording their infrared spectra (Table 1).

2.2. Spectral Measurements

The ^{1}H and ^{13}C NMR spectra of the 70 substances mentioned in Table 1 were measured using a BRUKER

Table 1. Melting points, N-H and C=O infrared absorption frequencies of *N*-(*j*,*k*-dichlorophenyl)- and *N*-(*j*,*k*-dimethylphenyl) substituted acetamides, *j*,*k*-$X'_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (X, X′ = Cl or CH_3; *i* =0, 1, 2 or 3). s: Strong.

j,*k*-X'_2, $CH_{3-i}X_i$	Compound	M. p. (°C)	γ_{N-H}(str) (cm^{-1})	$\gamma_{C=O}$(str) (cm^{-1})
2,3-Cl_2, CH_3	*N*-(2,3-Dichlorophenyl)-acetamide	159	3288.4s	1662.5s
2,3-Cl_2, CH_2Cl	*N*-(2,3-Dichlorophenyl)-2-chloroacetamide	112	3240.2s	1639.4s
2,3-Cl_2, $CHCl_2$	*N*-(2,3-Dichlorophenyl)-2,2-dichloroacetamide	130	3301.9s	1689.5s
2,3-Cl_2, CCl_3	*N*-(2,3-Dichlorophenyl)-2,2,2-trichloroacetamide	72 – 73	3379.1s	1730.3s
2,3-Cl_2, CH_2CH_3	*N*-(2,3-Dichlorophenyl)-2-methylacetamide	106	3301.9s	1670.2s
2,3-Cl_2, $CH(CH_3)_2$	*N*-(2,3-Dichlorophenyl)-2,2-dimethylacetamide	98	3220.9s	1681.8s
2,3-Cl_2, $C(CH_3)_3$	*N*-(2,3-Dichlorophenyl)-2,2,2-trimethylacetamide	62	3313.5s	1658.7s
2,4-Cl_2, CH_3	*N*-(2,4-Dichlorophenyl)-acetamide	144	3282.6s	1651.0s
2,4-Cl_2, CH_2Cl	*N*-(2,4-Dichlorophenyl)-2-chloroacetamide	112 – 113	3220.9s	1654.8s
2,4-Cl_2, $CHCl_2$	*N*-(2,4-Dichlorophenyl)-2,2-dichloroacetamide	124	3290.3s	1651.0s
2,4-Cl_2, CCl_3	*N*-(2,4-Dichlorophenyl)-2,2,2-trichloroacetamide	71	3373.3s	1724.2s
2,4-Cl_2, CH_2CH_3	*N*-(2,4-Dichlorophenyl)-2-methylacetamide	117	3278.8s	1662.5s
2,4-Cl_2, $CH(CH_3)_2$	*N*-(2,4-Dichlorophenyl)-2,2-dimethylacetamide	125	3276.8s	1660.6s
2,4-Cl_2, $C(CH_3)_3$	*N*-(2,4-Dichlorophenyl)-2,2,2-trimethylacetamide	59 – 60	3301.9s	1660.6s
2,5-Cl_2, CH_3	*N*-(2,5-Dichlorophenyl)-acetamide	133	3267.2s	1589.2s
2,5-Cl_2, CH_2Cl	*N*-(2,5-Dichlorophenyl)-2-chloroacetamide	117 – 118	3290.3s	1651.0s
2,5-Cl_2, $CHCl_2$	*N*-(2,5-Dichlorophenyl)-2,2-dichloroacetamide	148 – 150	3303.8s	1668.3s
2,5-Cl_2, CCl_3	*N*-(2,5-Dichlorophenyl)-2,2,2-trichloroacetamide	72	3309.6s	1670.2s
2,5-Cl_2, CH_2CH_3	*N*-(2,5-Dichlorophenyl)-2-methylacetamide	119	3282.6s	1678.8s
2,5-Cl_2, $CH(CH_3)_2$	*N*-(2,5-Dichlorophenyl)-2,2-dimethylacetamide	133	3259.5s	1662.5s
2,5-Cl_2, $C(CH_3)_3$	*N*-(2,5-Dichlorophenyl)-2,2,2-trimethylacetamide	65 – 66	3317.3s	1666.4s
3,4-Cl_2, CH_3	*N*-(3,4-Dichlorophenyl)-acetamide	110	3298.0s	1674.1s
3,4-Cl_2, CH_2Cl	*N*-(3,4-Dichlorophenyl)-2-chloroacetamide	95 – 96	3301.9s	1674.1s
3,4-Cl_2, $CHCl_2$	*N*-(3,4-Dichlorophenyl)-2,2-dichloroacetamide	122	3294.2s	1658.7s
3,4-Cl_2, CCl_3	*N*-(3,4-Dichlorophenyl)-2,2,2-trichloroacetamide	140	3255.6s	1693.4s
3,4-Cl_2, CH_2CH_3	*N*-(3,4-Dichlorophenyl)-2-methylacetamide	115	3303.8s	1668.3s
3,4-Cl_2, $CH(CH_3)_2$	*N*-(3,4-Dichlorophenyl)-2,2-dimethylacetamide	122	3238.3s	1664.5s
3,4-Cl_2, $C(CH_3)_3$	*N*-(3,4-Dichlorophenyl)-2,2,2-trimethylacetamide	145	3282.6s	1654.8s
3,5-Cl_3, CH_3	*N*-(3,5-Dichlorophenyl)-acetamide	180	3215.1s	1691.5s
3,5-Cl_2, CH_2Cl	*N*-(3,5-Dichlorophenyl)-2-chloroacetamide	137 – 138	3267.2s	1654.8s
3,5-Cl_2, $CHCl_2$	*N*-(3,5-Dichlorophenyl)-2,2-dichloroacetamide	142	3201.6s	1658.7s
3,5-Cl_2, CCl_3	*N*-(3,5-Dichlorophenyl)-2,2,2-trichloroacetamide	110	3282.0s	1662.5s
3,5-Cl_2, CH_2CH_3	*N*-(3,5-Dichlorophenyl)-2-methylacetamide	118	3313.5s	1670.2s
3,5-Cl_2, $CH(CH_3)_2$	*N*-(3,5-Dichlorophenyl)-2,2-dimethylacetamide	115	3263.3s	1662.5s
3,5-Cl_2, $C(CH_3)_3$	*N*-(3,5-Dichlorophenyl)-2,2,2-trimethylacetamide	155	3305.8s	1662.5s
2,3-$(CH_3)_2$, CH_3	*N*-(2,3-Dimethylphenyl)-acetamide	140	3236.3s	1658.7s
2,3-$(CH_3)_2$, CH_2Cl	*N*-(2,3-Dimethylphenyl)-2-chloroacetamide	128 – 129	3267.2s	1662.5s
2,3-$(CH_3)_2$, $CHCl_2$	*N*-(2,3-Dimethylphenyl)-2,2-dichloroacetamide	168	3253.7s	1674.1s
2,3-$(CH_3)_2$, CCl_3	*N*-(2,3-Dimethylphenyl)-2,2,2-trichloroacetamide	92 – 93	3269.1s	1683.7s
2,3-$(CH_3)_2$, CH_2CH_3	*N*-(2,3-Dimethylphenyl)-2-methylacetamide	105	3282.6s	1654.8s
2,3-$(CH_3)_2$, $CH(CH_3)_2$	*N*-(2,3-Dimethylphenyl)-2,2-dimethylacetamide	128 – 130	3273.0s	1656.7s
2,3-$(CH_3)_2$, $C(CH_3)_3$	*N*-(2,3-Dimethylphenyl)-2,2,2-trimethylacetamide	120	3259.5s	1651.0s
2,4-$(CH_3)_2$, CH_3	*N*-(2,4-Dimethylphenyl)-acetamide	133	3263.2s	1666.4s
2,4-$(CH_3)_2$, CH_2Cl	*N*-(2,4-Dimethylphenyl)-2-chloroacetamide	144 – 146	3255.6s	1658.7s
2,4-$(CH_3)_2$, $CHCl_2$	*N*-(2,4-Dimethylphenyl)-2,2-dichloroacetamide	162	3274.9s	1662.5s
2,4-$(CH_3)_2$, CCl_3	*N*-(2,4-Dimethylphenyl)-2,2,2-trichloroacetamide	140	3290.3s	1689.5s
2,4-$(CH_3)_2$, CH_2CH_3	*N*-(2,4-Dimethylphenyl)-2-methylacetamide	131	3274.9s	1651.0s
2,4-$(CH_3)_2$, $CH(CH_3)_2$	*N*-(2,4-Dimethylphenyl)-2,2-dimethylacetamide	138 – 139	3263.3s	1651.0s
2,4-$(CH_3)_2$, $C(CH_3)_3$	*N*-(2,4-Dimethylphenyl)-2,2,2-trimethylacetamide	194 – 195	3282.6s	1651.0s
2,5-$(CH_3)_2$, CH_3	*N*-(2,5-Dimethylphenyl)-acetamide	142	3278.8s	1662.5s
2,5-$(CH_3)_2$, CH_2Cl	*N*-(2,5-Dimethylphenyl)-2-chloroacetamide	152	3286.5s	1643.2s
2,5-$(CH_3)_2$, $CHCl_2$	*N*-(2,5-Dimethylphenyl)-2,2-dichloroacetamide	145	3251.8s	1678.0s
2,5-$(CH_3)_2$, CCl_3	*N*-(2,5-Dimethylphenyl)-2,2,2-trichloroacetamide	82	3301.9s	1662.5s
2,5-$(CH_3)_2$, CH_2CH_3	*N*-(2,5-Dimethylphenyl)-2-methylacetamide	125	3282.6s	1651.0s
2,5-$(CH_3)_2$, $CH(CH_3)_2$	*N*-(2,5-Dimethylphenyl)-2,2-dimethylacetamide	155 – 156	3278.8s	1658.7s
2,5-$(CH_3)_2$, $C(CH_3)_3$	*N*-(2,5-Dimethylphenyl)-2,2,2-trimethylacetamide	94	3272.5s	1662.5s
3,4-$(CH_3)_2$, CH_3	*N*-(3,4-Dimethylphenyl)-acetamide	95	3290.3s	1664.5s

Table 1 (continued).

j,*k*-X'_2, $CH_{3-i}X_i$	Compound	M. p. (°C)	γ_{N-H}(str) (cm^{-1})	$\gamma_{C=O}$(str) (cm^{-1})
3,4-$(CH_3)_2$, CH_2Cl	*N*-(3,4-Dimethylphenyl)-2-chloroacetamide	108	3294.2s	1670.2s
3,4-$(CH_3)_2$, $CHCl_2$	*N*-(3,4-Dimethylphenyl)-2,2-dichloroacetamide	162	3278.8s	1658.7s
3,4-$(CH_3)_2$, CCl_3	*N*-(3,4-Dimethylphenyl)-2,2,2-trichloroacetamide	124	3294.2s	1651.0s
3,4-$(CH_3)_2$, CH_2CH_3	*N*-(3,4-Dimethylphenyl)-2-methylacetamide	114	3288.4s	1660.6s
3,4-$(CH_3)_2$, $CH(CH_3)_2$	*N*-(3,4-Dimethylphenyl)-2,2-dimethylacetamide	137	3276.8s	1658.7s
3,4-$(CH_3)_2$, $C(CH_3)_3$	*N*-(3,4-Dimethylphenyl)-2,2,2-trimethylacetamide	130	3244.1s	1634.5s
3,5-$(CH_3)_2$, CH_3	*N*-(3,5-Dimethylphenyl)-acetamide	148	3301.9s	1662.5s
3,5-$(CH_3)_2$, CH_2Cl	*N*-(3,5-Dimethylphenyl)-2-chloroacetamide	152	3298.0s	1666.4s
3,5-$(CH_3)_2$, $CHCl_2$	*N*-(3,5-Dimethylphenyl)-2,2-dichloroacetamide	142	3251.8s	1612.4s
3,5-$(CH_3)_2$, CCl_3	*N*-(3,5-Dimethylphenyl)-2,2,2-trichloroacetamide	110	3367.5s	1608.5s
3,5-$(CH_3)_2$, CH_2CH_3	*N*-(3,5-Dimethylphenyl)-2-methylacetamide	128	3309.6s	1670.2s
3,5-$(CH_3)_2$, $CH(CH_3)_2$	*N*-(3,5-Dimethylphenyl)-2,2-dimethylacetamide	143	3244.0s	1651.0s
3,5-$(CH_3)_2$, $C(CH_3)_3$	*N*-(3,5-Dimethylphenyl)-2,2,2-trimethylacetamide	125	3298.0s	1654.8s

Table 2. Chemical shifts (δ, ppm) of various aromatic and other protons in *N*-(*j*,*k*-dichlorophenyl) substituted acetamides, *j*,*k*-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (X = Cl or CH_3; $i = 0$, 1, 2 or 3). s: Singlet; d: doublet; t: triplet; m: multiplet.

	2,3-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$					2,4-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$				
$COCH_{3-i}X_i$	H-4	H-5	H-6	N-H	Alkyl H	H-3	H-5	H-6	N-H	Alkyl H
$COCH_3$	7.27m	7.33m	7.84m	9.33	2.21	7.33d	7.16m	7.93d	8.60	2.16
$COCH_2Cl$	7.20d	7.26m	8.30m	8.97	4.23	7.40s	7.40s	7.40s	9.24	3.09
$COCHCl_2$	7.23d	7.29m	8.23m	8.85	6.08	7.01m	6.67s	7.23t	8.00	6.64
$COCCl_3$	7.07m	7.37m	7.98d	9.52	–	7.43d	7.31m	8.26d	8.98	–
$COCH_2CH_3$	7.19t	7.23t	8.32t	7.71	2.47, 1.26	7.36d	7.24m	8.35d	7.59	2.46, 1.27
$COCH(CH_3)_2$	7.16s	7.18s	8.30t	7.80	2.61, 1.28	7.36d	7.24m	8.35d	7.65	2.59, 1.27
$COC(CH_3)_3$	7.17d	7.20t	8.35m	8.07	1.35	7.33d	7.20m	8.34d	7.94	1.33
H	6.73	6.84	6.47	–	–	7.07	7.07	6.64	–	–
	2,5-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$					2,6-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$ [4]				
$COCH_{3-i}X_i$	H-3	H-4	H-6	N-H	Alkyl H	H-3,5	H-4	–	N-H	Alkyl H
$COCH_3$	7.28d	7.01m	8.04d	8.89	2.17	7.27d	7.08t	–	8.93	2.12
$COCH_2Cl$	7.28d	7.04m	8.37d	8.91	4.23	7.35d	7.18t		8.00	4.21
$COCHCl_2$	7.35d	7.11m	8.11d	9.50	6.55	7.40d	7.25t		10.2	6.42
$COCCl_3$	7.33d	7.11m	8.33d	8.96	–	7.35d	7.21t		8.16	–
$COCH_2CH_3$	7.21d	6.95m	8.39d	7.71	2.45, 1.23	7.40t	7.07t		7.93	2.55, 2.35, 1.14
$COCH(CH_3)_2$	7.26d	6.99m	8.51d	7.70	2.60, 1.28	7.14d	6.96t		8.05	2.60, 1.13
$COC(CH_3)_3$	7.25d	6.98m	8.51d	7.98	1.33	7.23d	7.06t		7.51	1.26
H	7.05	6.59	6.59	–	–	7.12	6.87		4.37	–
	3,4-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$					3,5-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$				
$COCH_{3-i}X_i$	H-2	H-5	H-6	N-H	Alkyl H	H-2,6	H-4	–	N-H	Alkyl H
$COCH_3$	7.63d	7.31d	7.43m	9.57	2.14	7.61s	6.99s	–	10.1	2.12
$COCH_2Cl$	7.81d	7.35t	7.40t	9.41	4.16	7.52d	7.16t		8.24	4.18
$COCHCl_2$	7.91d	7.36d	7.47m	10.4	6.33	7.65d	7.11t		10.7	6.36
$COCCl_3$	7.91d	7.38d	7.56m	10.0	–	7.75t	7.14t		10.3	–
$COCH_2CH_3$	7.98d	7.30d	7.49m	9.91	2.39, 1.17	7.47d	7.04t		8.31	2.41, 1.22
$COCH(CH_3)_2$	7.99d	7.39m	7.51m	9.65	2.62, 1.19	7.49d	7.04t		8.24	2.56, 1.21
$COC(CH_3)_3$	8.47s	8.03s	8.22s	9.50	2.01	7.49d	7.06t		7.44	1.30
H	6.54	7.17	6.54	–	–					

Table 3. Chemical shifts (δ, ppm) of various aromatic and other protons in *N*-(*j*,*k*-dimethylphenyl) substituted acetamides, *j*,*k*-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (X = Cl or CH_3; $i = 0$, 1, 2 or 3). s: Singlet; d: doublet; t: triplet; m: multiplet.

	2,3-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$					2,4-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$				
$COCH_{3-i}X_i$	H-4	H-5	H-6	N-H	Alkyl H	H-3	H-5	H-6	N-H	Alkyl H
$COCH_3$	6.90s	6.92s	7.07s	8.03	2.45, 2.06, 1.09	6.80d	6.85s	7.13d	8.20	2.20, 2.02, 1.95
$COCH_2Cl$	7.05t	7.12d	7.52d	8.19	4.20, 2.29, 2.16	7.02d	7.24s	7.65d	8.14	4.19, 2.29, 2.23
$COCHCl_2$	7.05m	7.22t	7.47s	9.40	6.36, 3.39, 2.19	7.04d	7.25s	7.58m	8.00	6.05, 2.30, 2.26
$COCCl_3$	7.03m	7.07s	7.26m	8.38	2.24, 2.07	7.04d	7.10s	7.13t	8.87	2.85, 2.10
$COCH_2CH_3$	6.96m	7.01s	7.24t	7.56	2.33, 2.26, 2.02, 1.17	6.91d	7.37s	7.41d	7.25	2.33, 2.23, 2.12, 1.76

Table 3 (continued).

	2,3-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$					2,4-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$				
$COCH_{3-i}X_i$	H-4	H-5	H-6	N-H	Alkyl H	H-3	H-5	H-6	N-H	Alkyl H
$COCH(CH_3)_2$	6.98d	7.07t	7.43d	7.25	2.55, 2.27, 2.11, 1.26	6.95d	7.15s	7.50d	7.25	2.52, 2.26, 2.16, 1.22
$COC(CH_3)_3$	6.97m	7.26s	7.29s	7.44	2.22, 2.01, 1.24	6.95m	7.00s	7.02d	7.29	2.15, 2.03, 1.19
H	6.53	6.82	6.34	–	–	6.74	6.74	6.36	–	–
	2,5-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$					2,6-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$ [4]				
$COCH_{3-i}X_i$	H-3	H-4	H-6	N-H	Alkyl H	H-3,5		H-4	N-H	Alkyl H
$COCH_3$	6.98d	6.83d	7.29s	7.74	2.22, 2.10, 2.05	6.90m		7.12t	7.74	2.20, 2.07, 2.00, 1.98, 1.85, 1.67
$COCH_2Cl$	7.03d	6.87d	7.25s	9.29	4.16, 2.25, 2.16	7.31t		7.16t	8.00	4.21, 1.57
$COCHCl_2$	6.99m	6.35d	7.35d	8.99	3.96, 2.14, 1.28	7.11d		7.08d	7.75	6.04, 2.22
$COCCl_3$	7.05d	6.93t	7.46s	8.31	2.28, 2.19	7.09m		7.09m	7.85	2.25
$COCH_2CH_3$	6.94s	6.92s	7.14d	7.81	2.25, 2.18, 1.96, 1.12	7.04d		6.88t	7.84	2.16, 2.0, 1.03
$COCH(CH_3)_2$	7.03d	6.86d	7.10s	7.59	2.53, 2.28, 2.17, 1.24	7.02m		7.02m	6.94	2.56, 2.15, 1.24, 1.02
$COC(CH_3)_3$	7.03d	6.85d	7.25d	7.66	2.29, 2.17, 1.31	6.99m		6.93t	7.25	2.04, 1.19
H	6.83	6.44	6.27	–	–	6.80		6.54	3.23	1.95
	3,4-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$					3,5-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$				
$COCH_{3-i}X_i$	H-2	H-5	H-6	N-H	Alkyl H	H-2,6	H-4	–	N-H	Alkyl H
$COCH_3$	7.22s	6.97d	7.25d	8.79	2.15, 2.13, 2.08	7.13s	6.67s	–	8.74	2.18, 2.08
$COCH_2Cl$	7.21d	7.03d	7.25t	8.38	4.09, 2.19, 2.09	7.33s	6.96s		8.46	4.29, 2.45
$COCHCl_2$	7.31m	7.06d	7.39s	9.93	6.34, 3.39, 2.22	7.17s	6.83s		8.12	6.03, 2.30
$COCCl_3$	7.29s	7.08d	7.33d	9.00	2.22, 1.84	7.22s	6.79s		9.34	2.26
$COCH_2CH_3$	6.89s	6.85d	7.18d	8.53	3.13, 2.26, 2.09, 1.12	7.14s	6.74s		7.25	2.34, 1.78, 1.22
$COCH(CH_3)_2$	7.21d	7.02d	7.32s	7.39	2.48, 2.19, 1.22, 1.20	7.17s	6.72s		7.40	2.47, 2.15, 1.26
$COC(CH_3)_3$	7.21m	7.02d	7.34d	7.41	2.20, 2.19, 1.28	7.18s	6.71s		7.46	2.25, 1.33
H						6.09	6.32		–	–

Table 4. Chemical shifts (δ, ppm) of various aromatic and other carbon atoms in *N*-(*j*,*k*-dichlorophenyl) substituted acetamides, *j*,*k*-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (X = Cl or CH_3; $i = 0$, 1, 2 or 3).

	2,3-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$							
$COCH_{3-i}X_i$	C-1	C-2	C-3	C-4	C-5	C-6	C=O	Alkyl C
$COCH_3$	136.7	125.5	131.7	124.2	126.9	123.2	168.2	23.0
$COCH_2Cl$	135.3	126.1	133.0	122.1	127.9	119.2	164.0	43.1
$COCHCl_2$	134.8	126.6	133.1	122.6	128.0	119.4	161.8	66.9
$COCCl_3$	136.1	127.6	134.3	127.3	132.8	119.8	159.3	94.1
$COCH_2CH_3$	136.3	125.1	132.6	123.1	127.8	119.5	172.0	31.0, 9.5
$COCH(CH_3)_2$	136.3	125.0	132.5	121.4	127.7	119.6	175.2	36.9, 19.5
$COC(CH_3)_3$	136.4	124.9	132.5	121.5	127.8	119.3	176.7	40.3, 27.5
H	144.4	119.0	132.4	116.8	127.3	113.5	–	–
$COCH_{3-i}X_i$	2,4-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$							
$COCH_3$	133.3	126.7	128.1	128.9	125.1	124.3	168.3	23.2
$COCH_2Cl$	134.0	127.8	130.2	133.2	126.3	125.1	164.5	41.8
$COCHCl_2$	141.7	122.8	127.7	128.9	119.6	116.4	165.0	69.3
$COCCl_3$	131.7	128.3	129.1	131.1	124.7	122.0	159.1	92.5
$COCH_2CH_3$	133.4	122.3	127.9	128.7	126.5	120.3	171.9	31.0, 9.5
$COCH(CH_3)_2$	133.4	127.9	128.6	128.9	123.2	122.3	175.1	36.9, 19.5
$COC(CH_3)_3$	133.4	127.7	128.3	128.6	123.3	122.0	176.4	40.0, 27.4
H	141.7	119.5	128.9	122.8	127.7	116.4	–	–
$COCH_{3-i}X_i$	2,5-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$							
$COCH_3$	135.7	123.3	129.5	124.3	131.8	122.7	168.4	23.2
$COCH_2Cl$	134.4	121.4	129.6	125.1	133.2	121.1	163.8	42.8
$COCHCl_2$	133.9	123.0	129.6	125.6	132.5	122.7	161.9	66.1
$COCCl_3$	133.9	122.2	129.9	126.3	133.8	121.4	159.0	92.5
$COCH_2CH_3$	135.4	121.6	129.4	124.2	133.2	120.8	171.8	30.7, 9.2
$COCH(CH_3)_2$	135.5	121.4	129.5	124.3	133.5	120.6	175.2	36.9, 19.5
$COC(CH_3)_3$	135.6	121.2	129.4	124.2	133.6	120.9	176.6	40.2, 27.4
H	143.7	118.5	129.9	117.8	132.8	115.5	–	–

Table 5. Chemical shifts (δ, ppm) of various aromatic and other carbon atoms in *N*-(*j*,*k*-dichlorophenyl) substituted acetamides, *j*,*k*-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (X = Cl or CH_3; $i = 0$, 1, 2 or 3).

2,6-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$ [4]								
$COCH_{3-i}X_i$	C-1	C-2,6	C-3,5	C-4	–	–	C=O	Alkyl C
$COCH_3$	133.8	127.9	127.8	127.8	–	–	169.0	22.3
$COCH_2Cl$	133.9	128.6	129.9	128.6			164.6	42.6
$COCHCl_2$	133.7	130.8	128.0	128.7			162.2	65.9
$COCCl_3$	134.0	130.5	128.7	129.6			159.6	92.4
$COCH_2CH_3$	134.8	126.0	128.7	128.0			172.6	31.0, 29.1, 9.6, 8.5
$COCH(CH_3)_2$	133.7	127.8	127.5	–			175.8	34.9, 19.2
$COC(CH_3)_3$	133.8	128.1	126.1	126.1			176.5	39.3, 27.4
H	146.9	123.5	129.0	121.0			–	–
3,4-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$								
$COCH_{3-i}X_i$	C-1	C-2	C-3	C-4	C-5	C-6	C=O	Alkyl C
$COCH_3$	138.0	120.9	131.6	129.7	129.0	118.7	169.0	23.8
$COCH_2Cl$	136.8	121.6	132.2	130.1	127.5	119.3	164.8	42.9
$COCHCl_2$	131.9	121.5	136.7	130.0	127.4	119.3	162.1	66.5
$COCCl_3$	132.1	122.6	136.2	130.0	128.3	120.3	159.7	92.6
$COCH_2CH_3$	138.7	123.4	133.0	129.7	131.0	119.6	172.7	29.7, 9.21
$COCH(CH_3)_2$	138.6	123.9	132.7	131.2	129.5	119.7	176.0	35.2, 19.0
$COC(CH_3)_3$	137.5	121.9	132.6	130.3	127.3	119.5	176.9	39.7, 27.5
H	146.1	116.3	132.5	120.8	130.6	114.6	–	–
3,5-$Cl_2C_6H_3NH$-CO-$CH_{3-i}X_i$								
$COCH_{3-i}X_i$	C-1	C-2,6		C-3,5		C-4	C=O	Alkyl C
$COCH_3$	140.9	117.3		134.2		122.4	169.2	23.9
$COCH_2Cl$	138.5	118.3		135.5		125.3	164.0	42.8
$COCHCl_2$	139.4	117.9		134.3		123.8	162.0	66.4
$COCCl_3$	138.8	119.1		134.5		124.7	159.7	92.5
$COCH_2CH_3$	139.8	118.4		135.1		124.1	173.3	30.6, 9.6
$COCH(CH_3)_2$	139.9	118.5		135.0		124.1	176.4	36.4, 19.5
$COC(CH_3)_3$	139.9	118.4		135.1		124.1	176.9	39.8, 27.5

Table 6. Chemical shifts (δ, ppm) of various aromatic and other carbon atoms in *N*-(*j*,*k*-dimethylphenyl) substituted acetamides, *j*,*k*-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (X = Cl or CH_3; $i = 0$, 1, 2 or 3).

2,3-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$								
$COCH_{3-i}X_i$	C-1	C-2	C-3	C-4	C-5	C-6	C=O	Alkyl C
$COCH_3$	137.0	130.7	135.5	125.2	127.3	123.2	169.2	23.0, 20.0, 13.5
$COCH_2Cl$	134.3	129.2	137.6	126.0	127.9	121.5	164.1	43.1, 20.5, 13.5
$COCHCl_2$	133.6	131.0	137.1	127.8	125.2	122.6	162.5	66.5, 19.9, 13.3
$COCCl_3$	133.3	130.6	137.6	128.6	125.8	122.1	159.9	92.9, 20.3, 13.4
$COCH_2CH_3$	137.1	130.2	135.3	125.5	127.3	122.8	172.7	29.9, 20.4, 13.6, 9.9
$COCH(CH_3)_2$	137.3	129.4	135.4	125.8	127.3	122.3	175.3	36.3, 20.5, 19.7, 13.6
$COC(CH_3)_3$	136.8	129.8	135.3	125.3	126.9	122.4	176.6	39.1, 27.4, 20.3, 13.3
H	144.3	125.5	136.4	120.0	125.5	112.7	–	–
$COCH_{3-i}X_i$	2,4-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$							
$COCH_3$	135.0	130.7	131.5	132.8	126.4	124.9	169.3	23.0, 20.5, 17.4
$COCH_2Cl$	135.6	129.5	131.2	132.0	127.4	122.8	163.9	43.1, 20.9, 17.4
$COCHCl_2$	131.4	127.6	130.2	136.4	126.5	123.2	162.1	67.1, 21.0, 17.4
$COCCl_3$	132.3	128.0	130.6	135.5	127.8	122.2	160.2	92.8, 20.3, 17.6
$COCH_2CH_3$	134.9	130.5	130.9	133.0	126.9	124.2	172.5	30.0, 20.7, 17.6, 9.9
$COCH(CH_3)_2$	134.8	129.9	131.0	133.0	127.1	123.8	175.3	36.2, 20.8, 19.7, 17.6
$COC(CH_3)_3$	135.4	127.7	131.8	134.2	126.7	124.2	176.6	38.9, 27.5, 20.1, 18.0
H	141.8	121.8	130.7	130.7	126.8	114.6	–	–
$COCH_{3-i}X_i$	2,5-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$							
$COCH_3$	135.9	127.6	130.1	126.2	135.3	124.9	169.0	23.6, 20.8, 17.2
$COCH_2Cl$	135.1	128.3	129.9	126.2	134.8	125.0	164.6	42.7, 20.3, 16.9
$COCHCl_2$	135.9	128.1	130.1	126.9	133.7	124.5	162.8	66.6, 20.5, 16.2
$COCCl_3$	136.6	127.5	130.4	126.9	133.4	123.7	159.6	92.9, 20.9, 16.8
$COCH_2CH_3$	137.0	127.2	130.5	125.3	135.3	123.0	172.9	29.7, 20.3, 13.6, 9.8
$COCH(CH_3)_2$	136.4	126.1	130.1	125.8	135.5	123.9	175.2	36.4, 21.0, 19.7, 17.2
$COC(CH_3)_3$	136.3	125.7	130.0	125.5	135.5	123.4	176.4	39.6, 27.6, 21.0, 17.1
H	144.2	118.8	129.9	118.8	136.0	115.3	–	–

Table 7. Chemical shifts (δ, ppm) of various aromatic and other carbon atoms in *N*-(*j*,*k*-dimethylphenyl) substituted acetamides, *j*,*k*-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (X = Cl or CH_3; i = 0, 1, 2 or 3).

2,6-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$ [4]								
$COCH_{3-i}X_i$	C-1	C-2,6	C-3,5	C-4	–	C=O	Alkyl C	
$COCH_3$	136.4	128.5	127.6	–			169.2	22.6, 19.7, 18.3
$COCH_2Cl$	135.2	132.8	128.1	127.5			164.6	42.6, 18.2
$COCHCl_2$	135.6	131.9	128.5	128.2			162.6	66.9, 18.1
$COCCl_3$	135.3	128.4	127.9	127.6			159.6	99.0, 42.8, 18.3
$COCH_2CH_3$	136.4	128.4	126.6	126.6			173.0	29.1, 25.2, 18.0, 10.0, 8.8
$COCH(CH_3)_2$	135.5	127.0	128.0	127.0			175.0	35.8, 8.3
$COC(CH_3)_3$	135.4	127.7	126.6	126.6			176.6	38.9, 27.5, 17.9
H	146.5	124.5	127.5	117.3			–	16.9
3,4-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$								
$COCH_{3-i}X_i$	C-1	C-2	C-3	C-4	C-5	C-6	C=O	Alkyl C
$COCH_3$	135.8	121.6	136.7	132.2	129.5	117.8	169.2	23.9, 19.6, 18.9
$COCH_2Cl$	133.5	121.6	137.2	134.3	129.9	117.8	164.1	42.9, 19.6, 19.1
$COCHCl_2$	132.8	121.0	136.6	134.6	129.4	117.3	161.6	66.7, 19.4, 18.7
$COCCl_3$	133.6	121.9	137.0	134.0	129.7	118.2	159.2	92.8, 19.5, 18.9
$COCH_2CH_3$	133.1	126.2	134.4	131.5	130.1	124.9	172.6	39.4, 29.2, 18.8, 9.6
$COCH(CH_3)_2$	135.9	121.5	137.1	132.4	129.9	117.6	175.3	36.5, 19.7, 19.6, 19.0
$COC(CH_3)_3$	135.7	121.5	136.9	132.3	129.7	117.6	176.5	39.4, 27.5, 19.7, 19.0
3,5-$(CH_3)_2C_6H_3NH$-CO-$CH_{3-i}X_i$								
$COCH_{3-i}X_i$	C-1	C-2,6	C-3,5	C-4	–	–	C=O	Alkyl C
$COCH_3$	138.2	118.1	138.0	125.8	–	–	169.1	23.9, 21.0
$COCH_2Cl$	136.5	117.9	138.8	126.9			163.9	42.9, 21.2
$COCHCl_2$	136.1	118.0	139.0	127.4			161.8	67.0, 21.3
$COCCl_3$	136.1	118.9	138.3	127.3			159.6	93.1, 21.1
$COCH_2CH_3$	138.7	117.6	136.9	126.0			159.5	30.9, 21.4, 9.7
$COCH(CH_3)_2$	138.6	117.7	138.0	125.8			175.4	36.6, 21.3, 19.6
$COC(CH_3)_3$	138.3	117.8	137.8	125.7			176.6	39.4, 27.5, 21.2
H	146.8	113.3	138.7	120.3			–	–

Ac 300F, 300 MHz FT-NMR spectrometer. The spectra were recorded in $CDCl_3$ and DMSO with tetramethylsilane (Me_4Si) as reference standard.

3. Results and Discussion

3.1. ^{1}H NMR Spectra

The assignments of the chemical shifts of the aromatic and other protons in all the 70 compounds are shown in Tables 2 and 3. These chemical shifts of aromatic protons were calculated in three different ways to check the validity of the principle of additivity of the substituent effects for this class of compounds: (i) by adding the substituent contributions [9, 10] to the corresponding ^{1}H chemical shifts of *N*-phenyl substituted acetamides, C_6H_5NH-CO-$CH_{3-i}X_i$ [5]; (ii) by adding the incremental shifts due to –NHCO$CH_{3-i}X_i$ groups [5] to the ^{1}H chemical shifts of protons of the corresponding *j*,*k*-dichlorobenzenes / *j*,*k*-dimethylbenzenes; (iii) by adding the incremental shifts due to –$COCH_{3-i}X_i$ groups [5] to the ^{1}H chemical shifts of protons of the corresponding *j*,*k*-dichloroanilines / *j*,*k*-dimethylanilines. This has been done by recording the ^{1}H NMR spectra of all the respective substituted benzenes and substituted anilines under identical conditions. Comparison of the three different sets of calculated values showed that all the three ways of calculation lead to almost the same values in most cases, and these values are in reasonable agreement with the measured chemical shifts of the aromatic protons.

3.2. ^{13}C NMR Spectra

The assignments of ^{13}C chemical shifts of aromatic and other carbon atoms in all 70 *N*-(*j*,*k*-dichlorophenyl)- and *N*-(*j*,*k*-dimethylphenyl)-acetamides and substituted acetamides are shown in Tables 4 – 7. The ^{13}C chemical shifts of aromatic carbon atoms in all *N*-(*j*,*k*-dichlorophenyl)- and *N*-(*j*,*k*-dimethylphenyl)-acetamides and substituted acetamides, *j*,*k*-$X'_2C_6H_3NH$-CO-$CH_{3-i}X_i$ (where *j*,*k* = 2,3; 2,4; 2,5; 3,4 or 3,5; X, X′ = CH_3 or Cl; i = 0, 1, 2 or 3) were also computed in three different ways, as described in 3.1. The comparison of the three sets of calculated values indicated that the three procedures of calculation lead to almost the same values in most cases and these values are in reasonable agreement with the experimental chemical shifts.

4. Comparisons and Conclusions

The overall comparison of all the calculated and observed chemical shifts of the aromatic protons and carbon atoms revealed that the chemical shifts calculated by adding the shifts due to either -NHCOCH$_{3-i}$X$_i$ or –COCH$_{3-i}$X$_i$ groups to the chemical shifts of the corresponding aromatic protons or carbon atoms of the respective substituted benzenes or substituted anilines give relatively better correlations with the experimental chemical shifts than the values obtained by adding the shifts due to the substituents in the benzene or aniline ring to the chemical shifts of the *N*-(phenyl) substituted acetamides.

The variation of ^{1}H chemical shifts of the amide protons with changes in side chain -NHCOCH$_{3-i}$X$_i$ (X = CH$_3$ or Cl; i = 0, 1, 2 or 3) in all the *N*-(*j*,*k*-dichlorophenyl)- and *N*-(*j*,*k*-dimethylphenyl)-acetamides and substituted acetamides, *j*,*k*-X$'_2$C$_6$H$_3$-NH-CO-CH$_{3-i}$X$_i$ (*j*,*k* = 2,3; 2,4; 2,5; 3,4 or 3,5; X,X$'$ = CH$_3$ or Cl; i = 0, 1, 2 or 3) showed more or less the same trend. The variations of ^{13}C-1, ^{13}C-O and alkyl ^{13}C chemical shifts with changes in the side chain also showed similar trends (figures not shown). The introduction of Cl into the methyl group in the side chain generally decreases the chemical shifts of ^{13}C-O, while introduction of additional methyl groups increases them. The effects are non-uniform in the case of ^{13}C-1 and amide proton chemical shifts. The ^{13}C chemical shift of the methyl carbon atom increases with the introduction of either Cl or additional CH$_3$ groups into it. The changes in the aryl group has little effect on the chemical shift of the carbonyl carbon atom.

Acknowledgement

The authors thank the Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh-14, India, for the ^{1}H and ^{13}C NMR spectral measurements.

[1] B. T. Gowda and A. Weiss, Z. Naturforsch. **49a**, 695 (1994); B. T. Gowda, S. Dou, and A. Weiss, Z. Naturforsch. **51a**, 627 (1996); B. T. Gowda, D. K. Bhat, H. Fuess, and A. Weiss, Z. Naturforsch. **54a**, 261, 679 (1999); B. T. Gowda, B. H. A. Kumar, and H. Fuess, Z. Naturforsch. **55a**, 721 (2000).

[2] B. T. Gowda, H. Paulus, and H. Fuess, Z. Naturforsch. **55a**, 711, 791 (2000); **56a**, 386 (2001); B. T. Gowda, I. Svoboda, and H. Fuess, Z. Naturforsch. **55a**, 779 (2000); **59a**, 845 (2004); B. T. Gowda, K. Jyothi, H. Paulus, and H. Fuess, Z. Naturforsch. **58a**, 225 (2003); B. T. Gowda, J. Kožìšek, and H. Fuess, Z. Naturforsch. **61a**, 588 (2006); B. T. Gowda, H. Paulus, J. Kožìšek, M. Tokarcik, and H. Fuess, Z. Naturforsch. **61a**, 675 (2006).

[3] B. T. Gowda, K. M. Usha, and K. L. Jayalakshmi, Z. Naturforsch. **58a**, 801 (2003).

[4] B. T. Gowda, K. M. Usha, and K. Jyothi, Z. Naturforsch. **59a**, 69 (2004).

[5] B. T. Gowda, Shilpa, and J. K. Lakshmipathy, Z. Naturforsch. **61a**, 595 (2006).

[6] W. A. Jacobs and M. Heidelberger, J. Biol. Chem. **21**, 104 (1915).

[7] A. J. Hill and E. B. Kelsey, J. Am. Chem. Soc. **44**, 2357 (1922).

[8] W. Pies, H. Rager, and A. Weiss, Org. Mag. Reson. **3**, 147 (1971).

[9] R. M. Silverstein, G. C. Bassler, and T. C. Morrill, Spectrometric Identification of Organic Compounds, Wiley, New York 1991.

[10] W. Kemp, Organic Spectroscopy, MacMillan, London 1996.