Infrared, ^{1}H and ^{13}C NMR Spectral Studies on Di- and Tri-substituted N-Aryl Amides, 2,6-$X_2C_6H_3NHCOCH_{3-i}X_i$ and 2,4,6-$X_3C_6H_2NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and i = 0, 1, 2 or 3)

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Several di- and tri-substituted amides of the general formula, 2,6-$X_2C_6H_3NHCOCH_{3-i}X_i$ and 2,4,6-$X_3C_6H_2NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2, or 3) are prepared, characterised, and their infrared spectra in the solid state and ^{1}H and ^{13}C NMR spectra in solution are studied. The C=O stretching vibrations of N-(2,6-dichlorophenyl)- and N-(2,6-dimethylphenyl)-amides appear as strong absorptions in the ranges 1707 – 1658 cm^{-1} and 1700 – 1647 cm^{-1}, respectively, while the N-H stretching vibrations of N-(2,6-dichlorophenyl)- and N-(2,6-dimethylphenyl)-amides appear as strong vibrations in the ranges 3271 – 3209 cm^{-1} and 3285 – 3214 cm^{-1}, respectively. The N-H stretching vibrations of N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)- amides also appear as strong absorptions in the ranges 3370 – 3212 and 3283 – 3225 cm^{-1}, respectively, while those of the C=O vibrations appear in the ranges 1688 – 1617 and 1704 – 1647 cm^{-1}. The analysis of the C=O and N-H absorption frequencies of all amides of the general formula $X_iC_6H_{5-i}NHCOCH_{3-i}X_i$ (where X = Cl or CH_3, and $i = 0$, 1, 2 or 3) indicates that their variations do not show regular trends with substitution either in the phenyl ring or in the side chain. The chemical shifts of both the aromatic protons and the aromatic carbons of all the amides are calculated in two ways, either by adding the incremental shifts due to -$COCH_{3-i}X_i$ groups and the substituents in the benzene ring to the chemical shifts of the corresponding aromatic protons or carbons of the parent aniline, or by adding the incremental shifts due to -$NHCOCH_{3-i}X_i$ groups and the substituents in the benzene ring to the chemical shift of the benzene proton or carbon. The calculated chemical shifts of the aromatic protons and carbons of all the substituted amides by both methods lead to almost the same values in most cases and agree well with the observed chemical shifts, indicating that the principle of additivity of the substituent effects is valid in these compounds.

Key words: Substituted Aryl Acetamides; Infrared; ^{1}H and ^{13}C NMR Spectra.

1. Introduction

Amides are of fundamental chemical interest as conjugation between nitrogen lone pair electrons and the carbonyl π-bond results in distinctive physical and chemical properties [1]. The amide moiety is an important constituent of many biologically significant compounds. Many imides, hydroxamic acids and hydrazides exhibit pharmacological activity which has further stimulated interest in their chemistry. Further, many acetanilides exhibit fungicidal, herbicidal and pharmacological activities. We have recently reported the infrared, Raman [2] and NQR [3] spectra and crystal structures [4] of several substituted N-(aryl)-chloroacetamides of the formula $XC_6H_5NHCOCH_{3-i}Cl_i$ (where X = H, o/m/p-CH_3, Cl or NO_2, and $i = 1$, 2 or 3), and the NMR spectra of N-(phenyl)- and N-(2/4-chlorophenyl or 2/4-methylphenyl)-substituted acetamides [5] of the formulae $C_6H_5NHCOCH_{3-i}X_i$ and 2/4-$XC_6H_4NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3). We report here the infrared and NMR spectra of several di- and tri-substituted amides of the general formulae 2,6-X_2-$C_6H_3NHCOCH_{3-i}X_i$ and 2,4,6-$X_3C_6H_2NHCOCH_{3-i}X_i$ (where X = Cl or CH_3, and $i = 0$, 1, 2 or 3).

2. Experimental

2.1. Preparation and Characterisation of the Compounds

The N-(2,6-dichloro/2,6-dimethyl-phenyl) and N-(2,4,6-trichloro/2,4,6-trimethyl-phenyl)-substituted

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

	$CH_{3-i}X_i$ (X = Cl or CH_3 and i = 0, 1, 2 or 3)						
Ar	CH_3	CH_2Cl	$CHCl_2$	CCl_3	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$
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
2,6-$Cl_2C_6H_3$	102	170	172	152	81	152	172
2,4,6-$Cl_3C_6H_2$	215	182	187	80	78	68	–
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
2,6-$(CH_3)_2C_6H_3$	182 – 184	141	158	138	119	189	205
2,4,6-$(CH_3)_3C_6H_2$	212	165	160	118	154	148	184

Table 2. Infrared absorption frequencies (cm^{-1}) of amides of the configuration, 2,6-$Cl_2C_6H_3NHCOR$.

s = strong, m = medium and w = weak; [a] [2].

Assignment	2,6-$Cl_2C_6H_3NHCOR$, R =							
	H	CH_3[a]	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$	CH_2Cl[a]	$CHCl_2$[a]	CCl_3[a]
N-H (str)	3243.7 s	3235.0 s	3262.0 s	3228.3 s	3263.9 s	3209.0 s	3217.7 s	3270.7 s
C-H (Ar sym str)	3077.8 w	3183.9 s	3080.7 m	3065.3 m	3078.8 w			3079.8 w
	3062.4 w	3029.6 s		3021.9 s		3040.2 m	3046.0 m	
	3019.0 m						3012.3 w	
C-H (alk str)	2985.3 s		2982.4 s	2967.0 s	2972.7 s	2953.5 w		
	2942.8 s		2941.9 s	2932.2 m	2934.2 m		2920.7 w	–
	2883.1 m	2814.6 w	2876.3 m	2874.4 m	2871.5 m	2854.1 w	2851.2 w	
Combination	1941.0 w	1942.9 w		1961.3 w	1945.8 w			1937.1 w
bands	1871.6 w	1875.4 w		1875.4 w	1868.7 w	–	–	
		1801.2 w	1722.1 s	1788.7 w	1793.5 w			
C=O (str)	1669.1 s	1662.3 s	1670.1 s	1657.5 s	1657.5 s	1681.6 s	1691.3 s	1706.7 s
C=C	1571.7 s	1567.8 s	1568.8 s	1567.8 s	1566.9 s	1576.5 m	1576.5 s	1570.7 m
(Ar in-plane str)	1522.5 s	1531.2 s.9 s	1520.6 m	1527.4 s	1507.1 s	1535.1 s	1543.7 s	1511.9 s
	1455.0 s	1457.0 s	1450.2 s	1457.0 s	1451.2 s	1455.0 s	1453.1 s	1452.1 m
	1435.7 s	1432.9 s	1436.7 s	1438.6 s	1436.7 s	1438.6 s	1436.7 s	1438.6 s
C-N (str)	1367.3 s		1350.9 s	1382.7 m	1368.3 s	1326.8 m	1326.8 w	
	1272.8 s	1295.0 s	1273.8 s	1268.0 s	1277.6 m	1270.9 m	1266.0 w	1271.8 m
C-H	1099.2 s	1102.1 m	1106.9 s	1164.8 m	1173.5 s	1197.6 m	1184.2 w	1198.5 m
(Ar in-plane bend)	1016.3 m	1011.5 m	1079.9 m		1025.9 m		1021.1 w	
C-X (str)	1067.4 s	1037.5 m	1054.9 s	1102.1 s	1100.2 s	1099.2 w	1099.2 s	1105.0 m
C-H	787.8 s	787.8 s	785.9 s	783.9 s	787.8 s	790.7 s	774.3 m	777.2 s
(Ar out of-plane bend)	778.1 s	776.2 s		718.4 m	706.8 s	777.2 s		
C=C (Ar out of-plane bend)	431.0 m	425.2 m	468.6 m	453.2 m	475.4 m	442.6 w	486.9 w	451.3 m

acetamides were prepared from substituted anilines, substituted acetic acids (Aldrich, Germany) and thionyl chloride. The commercial anilines 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 (2,6-dichloroaniline, 2,6-dimethylaniline, 2,4,6-trichloroaniline or 2,4,6-trimethylaniline) were treated with mixtures of the 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 of thionyl chloride was hydrolysed by adding cold water dropwise under ice cold conditions. Produced HCl was removed by treating with excess 2M NaOH. The separated solids were filtered under suction, washed thoroughly with water and dried. The N-aryl substituted acetamides thus prepared were recrystallised from ethanol several times to constant melting points. The compounds have been characterized by determining their melting points (Table 1).

Table 3. Infrared absorption frequencies (cm^{-1}) of amides of the configuration, 2,6-$(CH_3)_2C_6H_3NHCOR$.

s = strong, m = medium and w = weak; [a] [2].

Assignment	2,6-$(CH_3)_2C_6H_3NHCOR$, R =						
	CH_3	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$	CH_2Cl[a]	$CHCl_2$[a]	CCl_3[a]
N-H (str)	3236.0 s	3272.6 s	3266.8 s	3270.7 s	3213.8 s	3246.6 s	3285.0 s
C-H(Ar sym str)	3044.1 w	3021.9 w	3023.8 w	3020.9 w	3036.4 m	3012.3 w	–
C-H (alk str)	2921.6 w	2970.8 w	2967.0 m	2959.2 m	2972.7 w	2923.6 w	–
	2856.1 w	2924.5 w	2926.5 w	2924.5 w	2922.6 w	2854.1 w	
			2872.5 w	2870.5 w	2852.2 w		
Combination bands	–	1846.5 w	–	–	–	1828.2 w	–
		1773.2 w					
C=O (str)	1649.8 s	1655.6 s	1655.6 s	1649.8 s	1646.6 s	1675.8 s	1700.0 s
C=C (Ar in-plane str)	1541.8 s	1524.5 s	1529.3 s	1512.9 s	1537.0 s	1541.8 s	1510.0 s
	1475.3 m	1475.3 m	1460.8 m	1477.2 m	1476.2 m	1472.4 m	
	1440.6 w	1437.7 w		1439.6 w	1431.9 w		
C-N (str)	1302.7 m	1370.2 w	1381.8 m	1366.3 m	1323.9 m	1331.6 w	
		1294.0 w	1265.1 w	1296.9 m			1265.0 m
C-H	1094.4 w	1074.2 w	1100.2 m	1091.5 w	1147.4 m	1175.4 w	1095.0 m
(Ar in-plane bend)	1041.4 w	1030.8 w	1036.6 w	1036.6 m	1029.8 w	1039.4 w	
C-H	768.5 s	764.6 s	763.7 s	764.6 s	761.7 s	772.4 w	775.0 s
(Ar out of-plane bend)	731.9 w	729.0 w	704.9 w	722.2 w	708.7 m		710.0 s
C=C	483.1 w	436.8 w	432.0 w	479.2 w	470.6 w	438.7 w	420.0 m
(Ar out of-plane bend)							

Table 4. Infrared absorption frequencies (cm^{-1}) of amides of the configuration 2,4,6-$Cl_3C_6H_2NHCOR$.

s = strong, m = medium and w = weak; [a] [2].

Assignment	2,4,6-$Cl_3C_6H_2NHCOR$, R =					
	CH_3[a]	CH_2CH_3	$CH(CH_3)_2$	CH_2Cl	$CHCl_2$[a]	CCl_3[a]
N-H (str)	3221.5 s	3369.0 s	3236.0 s	3370.0 s	3211.9 s	3345.0 s
C-H(Ar sym str)	3064.3 s	3079.8 w	3079.8 w	3078.8 m	3078.8 s	3078.8 m
	3015.2 s				3033.5 s	
C-H (alk str)		2923.6 w	2926.5 m			–
	2851.2 w		2852.2 w	2851.2 w	2859.0 w	
combination bands			–		1868.7 w	1861.9 w
	1745.3 w	1725.0 w		1772.3 w		
C=O (str)	1665.2 s	1617.0 s	1673.0 s	1617.0 s	1688.4 s	1660.0 s
C=C (Ar in-plane str)	1576.5 s	1572.7 m	1561.1 s	1571.7 s	1567.8 s	1572.7 s
	1525.4 s	1558.2 m	1512.9 s	1558.2 s	1533.1 s	1557.2 s
	1454.1 s	1470.5 s	1467.6 s	1470.5 s	1454.1 s	1470.5 s
		1419.4 w	1450.2 s		1432.9 m	
C-N (str)	1376.9 s	1394.3 s	1383.7 s	1394.3 s	1375.0 s	1394.3 s
	1294.0 s	1298.8 m	1267.0 m	1298.8 m	1332.6 m	1298.8 m
C-H (Ar in-plane bend)	1144.6 s	–	1100.2 m	1141.7 w	1180.2 s	–
	1011.5 m		1020.2 m		1135.6 m	
C-X (str)	1082.8 m	1074.2 m	1075.1 m	1073.2 s	1079.0 m	1074.2 m
C-H	786.8 s	785.9 m	803.2 m	785.9 s	797.4 s	785.9 s
(Ar out of-plane bend)		710.6 m		710.6 s		710.6 s
C=C	459.9 s	470.6 w	465.7 w	429.1 w	441.6 m	426.2 m
(Ar out of-plane bend)						

2.2. Spectral Measurements

The Infrared spectra were recorded on a JASCO-430 (Japan) FT/IR spectrometer. The resolution was set to 4 cm^{-1}, and the scanning range was from 400 to 4000 cm^{-1}. The spectra were measured in the solid state as pressed KBr pellets (13 mm).

The proton NMR spectra 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 were as follows: The spectral frequency (SF) was kept at 300.134 MHz, sweep width (SW) 6024.096, pulse width (PW) 8.0, relaxation delay

Table 5. Infrared absorption frequencies (cm^{-1}) of amides of the configuration 2,4,6-$(CH_3)_3C_6H_2NHCOR$.

s = strong, m = medium and w = weak; [a] [2].

Assignment	2,4,6-$(CH_3)_3C_6H_2NHCOR$, R =						
	CH_3	CH_2CH_3	$CH(CH_3)_2$	$C(CH_3)_3$	CH_2Cl[a]	$CHCl_2$[a]	CCl_3
N-H (str)	3236.0 s	3238.9 s	3261.0 s	3283.2 s	3233.1 s	3225.4 s	3270.7 s
C-H(Ar sym str)	3042.2 s	3026.7 m		–	3037.3 s	3040.2 m	
			3015.2 w			3014.2 m	3018.1 w
C-H (alk str)	2980.5 w	2971.8 m	2970.8 s	2956.3 s	2996.8 m		2976.6 w
	2919.7 m	2917.8 m	2920.7 m	2918.7 s	2920.7 m	2921.6 w	2920.7 m
	2859.0 w		2868.6 m	2868.6 s	2860.9 m	2863.8 w	2857.0 w
C=O (str)	1646.9 s	1656.6 s	1655.6 s	1646.9 s	1671.0 s	1676.8 s	1703.8 s
C=C (Ar in-plane str)	1541.8 s	1532.2 s	1523.5 s	1511.0 s	1539.9 s	1540.9 s	1508.1 s
	1485.9 s	1484.9 m	1484.9 s		1485.9 s	1482.0 m	
	1427.1 s	1457.9 m	1463.7 s	1438.6 m	1463.7 s	1447.3 w	1439.6 w
C-N (str)		1370.2 m	1375.0 s	1366.3 m			1375.0 w
	1291.1 s	1308.5 w	1307.5 m	1308.5 m	1332.6 s	1335.5 m	1338.4 w
C-H (Ar in-plane bend)	1042.3 s	1071.3 m	1099.2 s	1185.0 s	1176.4 m	1189.9 m	
	1015.3 s	1040.4 m	1038.5 m	1036.6 m	1040.4 m	1040.4 m	1034.6 w
C-H	739.6 m	738.6 w	788.7 m	778.1 m	763.7 m	735.7 m	
(Ar out of-plane bend)	717.4 s	714.5 s	714.5 s	715.5 m	711.6 s		703.9 s
C=C (Ar out of-plane bend)	497.5 s	511.0 w	413.7 m	445.5 w	494.7 m	497.5 m	499.5 m

Table 6. 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).

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

Ar	$CH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3)						
	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	1685.0 s	1673.0 s	1672.0 s	1695.0 s	1666.2 s	1661.4 s	1654.6 s
2-Cl C_6H_4	1664.3 s	1673.9 s	1679.7 s	1709.6 s	1664.3 s	1654.6 s	1665.2 s
2-CH_3 C_6H_4	1652.7 s	1637.0 s	1672.0 s	1705.0 s	1653.7 s	1653.7 s	1655.6 s
4-Cl C_6H_4	1674.1 w	1670.0 s	1681.0 s	1709.0 s	1666.4 s	1662.5 s	1658.7 s
4-CH_3 C_6H_4	1660.6 w	1676.0 s	1674.0 s	1695.0 s	1610.5 s	1658.7 s	1652.9 s
2,6-Cl_2 C_6H_3	1662.3 s	1681.6 s	1691.3 s	1706.7 s	1670.1 s	1657.5 s	1657.5 s
2,6-$(CH_3)_2$ C_6H_3	1649.8 s	1646.6 s	1675.8 s	1700.0 s	1655.6 s	1655.6 s	1649.8 s
2,4,6-Cl_3 C_6H_2	1665.2 s	1617.0 s	1688.4 s	1660.0 s	1617.0 s	1673.0 s	–
2,4,6-$(CH_3)_3$ C_6H_2	1646.9 s	1671.0 s	1676.8 s	1703.8 s	1656.6 s	1655.6 s	1646.9 s
	γ_{N-H} (str) (cm^{-1})						
C_6H_5	3305.0 s	3266.8 s	3269.7 s	3290.0 s	3258.1 s	3299.6 s	3312.1 s
2-Cl C_6H_4	3241.8 s	3266.8 s	3254.3 s	3299.6 s	3288.0 s	3242.7 s	3369.1 s
2-CH_3 C_6H_4	3222.5 s	3340.0 s	3254.3 s	3300.0 s	3280.3 s	3269.7 s	3346.9 s
4-Cl C_6H_4	3263.3 s	3270.0 s	3278.0 s	3262.0 s	3300.0 s	3296.1 s	3300.0 s
4-CH_3 C_6H_4	3290.3 s	3365.0 s	3211.0 s	3300.0 s	3267.2 s	3273.0 s	3305.8 s
2,6-Cl_2 C_6H_3	3235.0 s	3209.0 s	3217.7 s	3270.7 s	3262.0 s	3228.3 s	3263.9 s
2,6-$(CH_3)_2$ C_6H_3	3236.0 s	3213.8 s	3246.6 s	3285.0 s	3272.6 s	3266.8 s	3270.7 s
2,4,6-Cl_3 C_6H_2	3221.5 s	3370.0 s	3211.9 s	3345.0 s	3369.0 s	3236.0 s	–
2,4,6-$(CH_3)_3$ C_6H_2	3236.0 s	3233.1 s	3225.4 s	3270.7 s	3238.9 s	3261.0 s	3283.2 s

(RD) 1.0 sec, acquisition time (AQ) 1.360 sec, receiver gain (RG) 10, decoupling power (DP) 63L CPD, filter to suppress noise(LB) 0.0, reference value (SR) was set at 4125.36 ppm for H_2O internally. ^{13}C NMR spectra of all the compounds were also recorded in $CDCl_3$ and DMSO with tetramethylsilane as the external reference standard under the following experimental conditions: The spectral frequency (SF) was kept at 75.469 MHz, sweep width (SW) 22727.273, pulse width (PW) 5.0, relaxation delay (RD) 1.0 sec, acquisition time (AQ) 0.360 sec, receiver gain (RG) 400, decoupling power (DP) 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. Infrared Spectra

The infrared absorption frequencies of N-(2,6-dichlorophenyl)- and N-(2,6-dimethylphenyl)-, N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphen-

Table 7. Chemical shifts (δ, ppm) of various aromatic protons and other protons in N-(2,6-dichlorophenyl)-substituted acetamides, 2,6-$Cl_2C_6H_3NHCOCH_{3-i}$ X_i (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

$COCH_{3-i}X_i$		H-3,5			H-4		N-H	Alkyl H
	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	obs.
$COCH_3$	7.27d	7.20	7.20	7.08t	7.02	7.02	8.93	2.12
$COCH_2Cl$	7.35d	7.27	7.27	7.18t	7.10	7.07	8.00	4.21
$COCHCl_2$	7.40d	7.32	7.32	7.25t	7.17	7.17	10.2	6.42
$COCCl_3$	7.35d	7.33	7.33	7.21t	7.18	7.18	8.16	–
$COCH_2CH_3$	7.40t	7.22	7.27	7.07t	6.97	6.97	7.93	2.55, 2.35, 1.14
$COCH(CH_3)_2$	7.14d	7.26	7.26	6.96t	7.06	7.06	8.05	2.60, 1.13
$COC(CH_3)_3$	7.23d	7.22	7.26	7.06t	7.01	7.01	7.51	1.26
H	7.12		–	6.87		–	4.37	–

Table 8. Chemical shifts (δ, ppm) of various aromatic protons and other protons in N-(2,6-dimethylphenyl)-substituted acetamides, 2,6-$(CH_3)_2C_6H_3NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

$COCH_{3-i}X_i$		H-3,5			H-4		N-H	Alkyl H
	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	obs.
$COCH_3$	6.90m	7.05	6.95	7.12t	6.82	6.82	7.74	2.20, 2.07, 2.00, 1.98, 1.85, 1.67
$COCH_2Cl$	7.31t	7.02	7.02	7.16t	6.90	6.85	8.00	4.21, 1.57
$COCHCl_2$	7.11d	7.07	7.07	7.08d	6.97	6.97	7.75	6.04, 2.22
$COCCl_3$	7.09m	7.08	7.08	7.09m	6.98	7.01	7.85	2.25
$COCH_2CH_3$	7.04d	6.93	6.97	6.88t	6.77	6.77	7.84	2.16, 2.0, 1.03
$COCH(CH_3)_2$	7.02m	7.01	7.01	7.02m	6.86	6.86	6.94	2.56, 2.15, 1.24, 1.02
$COC(CH_3)_3$	6.99m	6.95	7.01	6.93t	6.81	6.81	7.25	2.04, 1.19
H	6.80		–	6.54		–	3.23	1.95

Table 9. Chemical shifts (δ, ppm) of various aromatic carbons and other carbons in N-(2,6-dichlorophenyl)-substituted acetamides, 2,6-$Cl_2C_6H_3NHCOCH_{3-i}X_i$ (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=O	Alkyl C
	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	obs.
$COCH_3$	133.8	138.0	138.5	127.9	127.8	127.8	127.8	126.7	126.7	127.8	126.0	126.0	169.0	22.3
$COCH_2Cl$	133.9	137.2	137.7	128.6	127.8	127.8	129.9	126.9	127.8	128.6	127.1	127.1	164.6	42.6
$COCHCl_2$	133.7	136.6	137.1	130.8	128.0	128.5	128.0	127.4	127.9	128.7	125.8	128.3	162.2	65.9
$COCCl_3$	134.0	136.3	136.3	130.5	128.0	128.0	128.7	127.3	127.5	129.6	128.0	128.0	159.6	92.4
$COCH_2CH_3$	134.8	139.4	139.4	126.0	126.7	126.7	128.7	126.9	126.8	128.0	124.8	124.5	172.6	31.0, 29.1, 9.6, 8.5
$COCH(CH_3)_2$	133.7	138.6	138.6	127.8	127.4	127.5	127.5	127.0	127.0	–	126.0	126.1	175.8	34.9, 19.2
$COC(CH_3)_3$	133.8	138.5	138.5	128.1	127.8	127.8	126.1	126.5	126.5	126.1	125.7	125.7	176.5	39.3, 27.4
H	146.9		–	123.5		–	129.0		–	121.0		–	–	–

yl)- amides are given in Tables 2 – 5. The absorption frequencies of some of the related substituted amides have been included in the tables for comparison. The general assignments of the important frequencies to various modes are indicated in the tables. Assignment of various bands in various compounds, in general, has been dealt with in detail in [6 – 8]. This is not discussed here. The precise frequency or wavelength at which a specific group absorbs depends on its environment within the molecule and on its physical state.

The C=O stretching vibrations of N-(2,6-dichlorophenyl)- and N-(2,6-dimethylphenyl)-amides appear as strong absorptions in the ranges 1707 – 1658 cm^{-1} and 1700 – 1647 cm^{-1}, respectively, compared to the frequency ranges of 1695 – 1642 cm^{-1}, 1710 – 1653 cm^{-1}, 1705 – 1637 cm^{-1} observed for the N-(phenyl)-, N-(2-chlorophenyl)- and N-(2-methylphenyl)-amides, respectively. The N-H stretching vibrations of N-(2,6-dichlorophenyl)- and N-(2,6-dimethylphenyl)-amides also appear as strong vibrations in the ranges 3271 – 3209 cm^{-1} and 3285 – 3214 cm^{-1}, respectively, compared to the frequency ranges of 3337 – 3240 cm^{-1}, 3369 – 3242 cm^{-1} and 3347 – 3223 cm^{-1}, observed for the N-(phenyl)-,

Table 10. Chemical shifts (δ, ppm) of various aromatic carbons and other carbons in N-(2,6-dimethylphenyl)-substituted acetamides, 2,6-$(CH_3)_2C_6H_3NHCOCH_{3-i}X_i$ (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=O	Alkyl C
	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	obs.
$COCH_3$	136.4	139.0	139.5	128.5	129.6	127.8	127.6	126.3	126.5	–	123.8	122.7	169.2	22.6, 19.7,18.3
$COCH_2Cl$	135.2	138.2	138.2	132.8	129.6	129.6	128.1	126.5	128.7	127.5	124.9	124.9	164.6	42.6, 18.2
$COCHCl_2$	135.6	137.6	138.1	131.9	129.8	130.3	128.5	127.0	127.5	128.2	125.6	125.6	162.6	66.9, 18.1
$COCCl_3$	135.3	137.3	137.3	128.4	129.8	129.8	127.9	126.9	126.9	127.6	125.8	125.8	159.6	99.0, 42.8, 18.3
$COCH_2CH_3$	136.4	139.9	140.4	128.4	128.5	128.5	126.6	126.5	126.4	126.6	122.6	122.3	173.0	29.1, 25.2, 18.0, 10.0, 8.8
$COCH(CH_3)_2$	135.5	139.6	139.6	127.0	129.2	129.3	128.0	126.6	126.6	127.0	123.8	123.9	175.0	35.8, 8.3
$COC(CH_3)_3$	135.4	139.5	139.6	127.7	129.6	129.7	126.6	126.1	126.1	126.6	123.5	123.6	176.6	38.9, 27.5, 17.9
H	146.5		–	124.5		–	127.5		–	117.3		–	–	16.9

Table 11. Chemical shifts (δ, ppm) of various aromatic protons in N-(2,4,6-trichlorophenyl)-substituted acetamides, 2,4,6-$Cl_3C_6H_4NHCOCH_{3-i}X_i$ (X = Cl or CH_3 and $i = 0$, 1, 2 or 3).

$COCH_{3-i}$ X_i	H-3,5			N-H	Alkyl H
	obs.	calc. 1	calc. 2	obs.	obs.
$COCH_3$	7.32d	7.20	7.20	8.94	2.05
$COCH_2Cl$	7.40	7.27	7.27	8.02	4.21
$COCHCl_2$	7.42d	7.32	7.32	7.91	6.08
$COCCl_3$	7.14d	7.33	7.33	4.40	–
$COCH_2CH_3$	7.14d	7.22	7.27	7.93	2.55, 2.35, 1.14
$COCH(CH_3)_2$	7.12d	7.26	7.26	8.05	2.60, 1.13
H	7.15	7.22	–	4.4	–

Table 12. Chemical shifts (δ, ppm) of various aromatic protons in N-(2,4,6-trimethylphenyl)-substituted acetamides, 2,4,6-$(CH_3)_3C_6H_2NHCOCH_{3-i}X_i$, (X = Cl or CH_3 and $i =$ 0, 1, 2 or 3).

$COCH_{3-i}$ X_i	H-3,5			N-H	Alkyl H
	obs.	calc. 1	calc. 2	obs.	obs.
$COCH_3$	6.86d	6.80	6.80	6.70	2.05
$COCH_2Cl$	6.82s	6.87	6.87	9.37	4.14, 2.15
$COCHCl_2$	6.85m	6.92	6.92	9.56	6.38, 2.25, 2.15
$COCCl_3$	6.86d	6.93	6.93	7.85	2.35, 2.32, 2.28, 2.24, 2.19
$COCH_2CH_3$	6.78d	6.82	6.87	7.08	2.23, 2.03, 1.23
$COCH(CH_3)_2$	6.74m	6.86	6.86	7.28	2.50, 2.20, 2.01 1.14, 0.99
$COC(CH_3)_3$	6.78d	6.80	6.86	7.08	2.23, 2.03, 1.23
H	6.66		–	3.21	2.15, 2.01

Table 13. Chemical shifts (δ, ppm) of aromatic carbons in N-(2,4,6-trichlorophenyl)- substituted acetamides, 2,4,6-$Cl_3C_6H_2NHCOCH_{3-i}X_i$, (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=O	Alkyl C
	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	obs.
$COCH_3$	139.0	136.0	136.5	127.5	128.8	128.8	127.5	126.9	126.9	128.3	132.2	132.4	168.5	22.1
$COCH_2Cl$	134.4	135.2	135.2	129.9	128.8	128.8	128.6	131.1	126.9	134.4	133.5	133.5	164.4	42.6
$COCHCl_2$	134.3	134.6	134.6	130.0	129.0	129.0	127.9	127.6	127.2	134.2	134.2	134.7	162.4	65.7
$COCCl_3$	139.9	134.3	136.5	128.3	129.0	128.8	127.5	127.5	127.5	–	134.4	134.4	159.5	92.3
$COCH_2CH_3$	139.0	137.4	137.4	127.5	127.7	127.7	127.5	126.8	127.0	128.3	131.2	130.9	173.0	35.8, 18.3
$COCH(CH_3)_2$	139.0	136.6	136.5	128.2	128.4	128.8	127.5	127.2	127.2	128.2	131.8	132.1	175.0	35.7, 19.5
H	139.1		–	121.8		–	127.8		–	121.8		–		–

N-(2-chlorophenyl)- and N-(2-methylphenyl)-amides, respectively. The C-N stretching vibrations did not show regular trends with substitution in the side chain. This may be due to the fact that the spectra of the compounds are recorded in the solid state, and the compounds may crystallise in different crystalline forms. The other frequencies are assigned to various other vibrations of the ring (Tables 2 – 5).

The N-H stretching vibrations of N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)-amides appear as strong absorptions in the ranges 3370 – 3212 and 3283 – 3225 cm^{-1}, respectively. The C=O vibrations appear as strong absorptions in the ranges 1688 – 1617 and 1704 – 1647 cm^{-1} for N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)- amides, respectively. The C=O and N-H absorption frequencies of all the amides of the general formula $X_iC_6H_{5-i}NHCOCH_{3-i}X_i$ (where X = Cl or CH_3 and $i = 0$, 1, 2 or 3), namely, N-(phenyl)-, N-(2-chlorophenyl)-, N-(2-methylphenyl)-, N-(4-chlorophenyl)-, N-(4-methylphenyl)-, N-(2,6-dichlorophenyl)-, N-(2,6-dimethylphenyl)-, N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)-amides are shown in Table 6 [2]. It is evident from

Table 14. Chemical shifts (δ, ppm) of aromatic carbons in N-(2,4,6-trimethylphenyl)-substituted acetamides 2,4,6-$(CH_3)_3C_6H_2NHCOCH_{3-i}X_i$ (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=O	Alkyl C	
	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	calc. 1	calc. 2	obs.	obs.	
$COCH_3$	137.0	136.1	136.6	128.9	129.5	129.5	128.9	127.0	127.0	136.3	133.1	133.1	168.9	23.1, 21.0,18.3	
$COCH_2Cl$	135.8	135.3	135.3	131.3	129.5	129.5	128.2	127.2	127.4	134.7	134.2	134.2	164.7	42.4, 39.5, 20.4, 17.7	
$COCHCl_2$	134.6	134.7	134.7	129.9	129.7	129.7	128.2	127.7	127.7	136.4	134.9	134.9	162.4	66.4, 20.4,17.4	
$COCCl_3$	135.2	134.4	134.4	129.7	129.7	129.7	129.2	127.6	127.6	135.2	135.1	135.1	165.7	21.0, 20.7,17.9	
$COCH_2CH_3$	137.7	137.0	137.5	129.1	128.4	128.4	128.5	127.2	127.1	136.2	131.9	131.6	172.9	29.3, 20.8, 18.0, 10.2	
$COCH(CH_3)_2$	136.1	136.7	136.7	129.2	129.1	129.2	128.5	127.3	127.4	135.0	133.1	133.2	175.7	35.3, 20.84, 19.7, 17.99	
$COC(CH_3)_3$	136.1	136.6	136.6	131.5	129.5	129.6	128.5	126.8	126.8	135.0	132.8	133.0	176.6	39.0, 27.6, 20.8, 17.9	
H	139.9	–	–	121.3	–	–	128.5	–	–	126.4	–	–	–	20.0, 17.0	

Table 15. The incremental shifts in chemical shifts (δ, ppm) of aromatic protons due to -$COCH_{3-i}X_i$ and -NH $COCH_{3-i}X_i$ 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	0.1 7	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

Table 16. The incremental shifts in chemical shifts of aromatic carbons due to -$COCH_{3-i}X_i$ and -NH $COCH_{3-i}X_i$ 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

the comparison of these data that the C=O and N-H absorption frequencies did not show regular trends with the substitution either in the phenyl ring or in the side chain, although the C=O absorptions frequencies are generally higher for compounds with the trichloro group in the side chain.

3.2. ^{1}H and ^{13}C NMR Spectra

The chemical shifts of aromatic and other protons of N-(2,6-dichlorophenyl)- and N-(2,6-dimethylphenyl)-substituted acetamides are shown in Tables 7 and 8, and those of carbons are given in Tables 9 and 10. The ^{1}H and ^{13}C NMR chemical shifts of various aromatic and other protons and carbons of all the N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)- substituted acetamides are shown in Tables 11 – 14.

The chemical shifts of both the aromatic protons and carbons of all the N-(2,6-dichlorophenyl)-, N-(2,6-dimethylphenyl)-, N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)- substituted acetamides were calculated in two ways. In the first method, the chemical shifts of various aromatic protons and carbons in these compounds were computed by adding the shifts due to -$COCH_{3-i}X_i$ groups (Tables 15 and 16) [5] and the shifts due to the substituents (Tables 17 and 18) [7, 8] at different positions in the benzene ring to the chemical shifts of the corresponding aromatic protons or carbons of the parent aniline. In the second method, the chemical shifts of the aromatic protons and carbons of all the N-(2,6-dichlorophenyl)-, N-(2,6-

Table 17. Shifts in the position of benzene protons (δ7.27) 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

Table 18. 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 (Attachment)	C-2 C-2	C-3 C-3	C-4 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	–

dimethylphenyl)-, N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)- substituted acetamides were calculated by adding the shifts due to -$NHCOCH_{3-i}X_i$ groups (Tables 15 and 16) and the shifts due to the substituents (Tables 17 and 18) at different positions in the benzene ring to the chemical shift of the benzene proton or carbon.

The calculated chemical shifts of different aromatic protons and carbons of all the N-(2,6-dichlorophenyl)-, N-(2,6-dimethylphenyl)-, N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)- substituted acetamides by methods 1 and 2 compared with the observed chemical shifts are shown in Tables 7 – 14. The comparison of the two sets of calculated values of the chemical shifts showed that the two procedures of calculation lead to almost the same values in most cases, and these values agree well with the observed chemical shifts. This observation indicates that the principle of additivity of effects due to various groups is valid with all the N-(2,6-dichlorophenyl)-, N-(2,6-dichlorophenyl)- N-(2,4,6-trichlorophenyl)- and N-(2,4,6-trimethylphenyl)- substituted acetamides.

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