^{35}Cl NQR and Structural Studies of N-(2,6-Dichlorophenyl)-Amides, 2,6-$Cl_2C_6H_3$-NHCO-R (R = H or $CH_{3-y}X_y$ and X = CH_3 or Cl; y = 0, 1, 2 or 3)

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The effect of side chain substitution on the ^{35}Cl NQR and crystal structure of amides of the type N-(2,6-dichlorophenyl)-amides, 2,6-$Cl_2C_6H_3$-NHCO-R (R = H or $CH_{3-y}X_y$ where X = CH_3 or Cl and y = 0, 1, 2 or 3), has been studied by measuring the ^{35}Cl NQR spectra and determining the crystal structures of the compounds N-(2,6-dichlorophenyl)-formamide, 2,6-$Cl_2C_6H_3$-NHCO-H (**DCPFA**); N-(2,6-dichlorophenyl)-2-methylacetamide(propionamide), 2,6-$Cl_2C_6H_3$-NHCO-CH_2CH_3 (**DCPMA**); N-(2,6-dichlorophenyl)-2,2-dimethylacetamide(isobutyramide), 2,6-$Cl_2C_6H_3$-NHCO-$CH(CH_3)_2$ (**DCPDMA**) and N-(2,6-dichlorophenyl)-2,2,2-trimethylacetamide (neopentylamide), 2,6-$Cl_2C_6H_3$-NHCO-$C(CH_3)_3$ (**DCPTMA**), and by analysing the present data along with the ^{35}Cl NQR spectra and / or crystal structures of the compounds, 2,6-dichloroaniline, 2,6-$Cl_2C_6H_3$-NH_2 (**DCA**), N-(2,6-dichlorophenyl)-acetamide, 2,6-$Cl_2C_6H_3$-NHCO-CH_3 (**DCPA**), N-(2,6-dichlorophenyl)-2-chloroacetamide, 2,6-$Cl_2C_6H_3$-NHCO-CH_2Cl (**DCPCA**), N-(2,6-dichlorophenyl)-2,2-dichloroacetamide, 2,6-$Cl_2C_6H_3$-NHCO-$CHCl_2$ (**DCPDCA**) and N-(2,6-dichlorophenyl)-2,2,2-trichloroacetamide, 2,6-$Cl_2C_6H_3$-NHCO-CCl_3 (**DCPTCA**). The crystal type, space group, formula units and lattice constants in Å of the new structures are;**DCPFA**: orthorhombic, Pbca, Z = 8, a = 8.593(3), b = 12.728(4), c = 14.376(4); **DCPMA**: orthorhombic, $P2_12_12_1$, Z = 4, a = 4.774(2), b = 10.961(5), c = 19.562(8); **DCPDMA**: monoclinic, $P2_1/c$, Z = 4, a = 9.901(4), b = 13.785(5), c = 9.060(3), β = 103.58(2)° and **DCPTMA**: monoclinic, $P2_1/n$, Z = 8, a = 16.047(5), b = 9.882(3), c = 16.270(5) β = 102.12(1)°. The compound, **DCPTMA** shows two molecules in its asymmetric unit. This is in agreement with the multiple lines observed in the ^{35}Cl NQR spectra of the compound. The conversion of **DCA** (monoclinic) into it's various acid amides **DCPFA, DCPA, DCPMA, DCPDMA, DCPTMA, DCPCA** and **DCPTCA** affects it's crystal symmetry. The replacement of the side chain CH_3 in **DCPA** by the H atom or substitution of either a CH_3 group or a Cl atom for one of the H atoms in the side chain CH_3 or replacement of the two ring Cl atoms by the H atoms changes it's crystal symmetry from monoclinic to orthorhombic, while the substitution of 2 or all the 3 H atoms in the CH_3 group of **DCPA** by 2 or 3 CH_3 groups or Cl atoms restores it's crystal symmetry back to the monoclinic type. The bond lengths and bond angles are normal except for some deviations.

Key words: ^{35}Cl NQR, Crystal Structures; N-2,6-dichlorophenyl-substitutedamides.

Introduction

The combined tool of NQR spectroscopy and crystal structure studies has been extensively used to investigate the structural aspects of a variety of compounds [1 - 3]. Amides are of fundamental chemical interest, as conjugation between the nitrogen lone pair electrons and the carbonyl π-bond results in distinct physical and chemical properties [4]. The amide moiety is an important constituent of many biologically significant compounds [4, 5]. We are thus interested in structural studies of amides in their crystalline state using this combined tool [6 - 15].

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Table 1. Ring C-Cl $^{35}Cl^{2,6}$ NQR frequencies of N-(2,6-dichlorophenyl)-amides, 2,6-$Cl_2C_6H_3$-NHCO-R, at 77 K and room temperature (295 K).

	$\nu(^{35}Cl^{2,6})$/MHz 77 K	S/N	$\nu(^{35}Cl^{2,6})$/MHz R.T. (295 K)	S/N	Ref.
2,6-$Cl_2C_6H_3$-NHCO-H (**DCPFA**)					
ν_1	35.936	30	35.396	20	present
ν_2	36.047	25	35.482	20	work
mean	35.992		35.439		
2,6-$Cl_2C_6H_3$-NHCO-CH_3 (**DCPA**)					
ν_1	35.866	20	35.184	10	[18]
ν_2	36.019	20	35.304	10	
mean	35.943		35.244		
2,6-$Cl_2C_6H_3$-NHCO-CH_2CH_3 (**DCPMA**)					
ν_1	35.580	25	34.793	15	present
ν_2	35.909	25	35.169	15	workt
mean	35.745				
2,6-$Cl_2C_6H_3$-NHCO-$CH(CH_3)_2$ (**DCPDMA**)					
ν_1	35.775	30	34.848	15	present
ν_2	35.775	30	34.848	15	work
mean	35.775		34.848		
2,6-$Cl_2C_6H_3$-NHCO-$C(CH_3)_3$ (**DCPTMA**)					
ν_1	35.611	20	34.659	10	present
ν_2	35.653	20	34.671	10	work
ν_3	35.802	20	34.779	10	
ν_4	35.889	15	34.882	10	
mean	35.739				
2,6-$Cl_2C_6H_3$-NHCO-CH_2Cl (**DCPCA**)					
ν_1	35.758	30	35.101	15	[17]
ν_2	36.186	30	35.554	15	
mean	35.972		35.328		
2,6-$Cl_2C_6H_3$-NHCO-$CHCl_2$ (**DCPDCA**)					
ν_1	35.960-	20	35.430-	10	[17]
ν_2	36.220	20	35.670	10	
mean	36.090		35.550		
2,6-$Cl_2C_6H_3$-NHCO-CCl_3 (**DCPTCA**)					
ν_1	36.267	30	35.609	10	[17]
ν_2	36.381	30	35.567	10	
mean	36.324		35.588		
2,6-$Cl_2C_6H_3$-NHCO-2,6-$Cl_2C_6H_3$-NH_2 (**DCA**)					
ν_1	34.403	20	33.517	10	[20]
ν_2	35.011	20	34.185	10	
mean	34.704		33.851		

The ^{35}Cl NQR spectra of a number of N-(chlorophenyl) chloroacetamides have been studied [16, 17]. We have recently prepared several substituted amides of the configuration $X_yC_6H_{5-y}$-NHCO-$CH_{3-y}Cl_y$ (where X = CH_3, NO_2 or Br and y = 1, 2 or 3) and measured their ^{35}Cl NQR and IR spectra [9 - 12]. Crystal structures of some of the N-phenyl acetamides have also been determined [7, 8, 13 - 15, 17, 18]. The emphasis is mainly on the ring substitution and substitution of Cl for H in the side chain. There are no reports of similar studies on other amides, to know the effect of introducing the electron donating groups in the side chain, as most of the studies are centred on chlorosubstituted N-phenyl acetamides. We have recently observed during investigations with -N-Cl compounds that the electron donating groups at the side chain substantially alter the ^{35}Cl NQR frequency of Cl(N) [6 - 8]. Hence we thought it interesting to measure the ^{35}Cl NQR frequencies and determine the crystal structure of various amides to see how the -NHCO- bond parameters vary on substitution of the electron donating groups in the side chain. Thus we report herein the ^{35}Cl NQR spectra and single crystal structures of

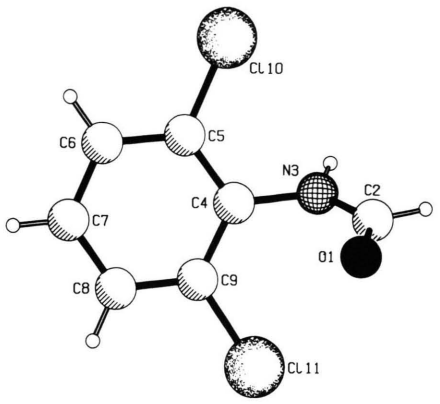

Fig. 1. Molecular geometry of N-(2,6-dichlorophenyl)-formamide, 2,6-$Cl_2C_6H_3$-NHCO-H (**DCPFA**), with the numbering of atoms.

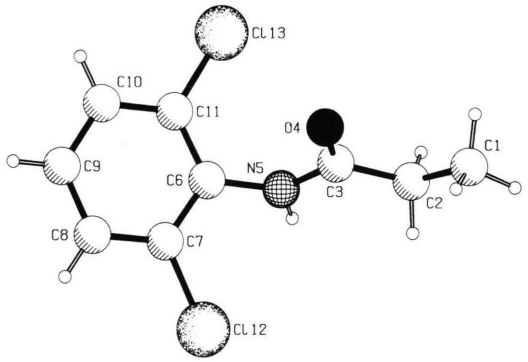

Fig. 2. Molecular geometry of N-(2,6-dichlorophenyl)-2-methylacetamide, 2,6-$Cl_2C_6H_3$-NHCO-CH_2CH_3 (**DCPMA**), with the numbering of atoms.

Table 2. Experimental conditions for the crystal structure determination and crystallographic data of 2,6-$Cl_2C_6H_3$-NHCO-H (**DCPFA**); 2,6-$Cl_2C_6H_3$-NHCO-CH_2CH_3 (**DCPMA**); 2,6-$Cl_2C_6H_3$-NHCO-$CH(CH_3)_2$ (**DCPDMA**) and 2,6-$Cl_2C_6H_3$-NHCO-$C(CH_3)_3$ (**DCPTMA**). Diffractometer: Stoe-Stadi 4; Monochromator: Graphite (002); scan/$2\theta/\omega$ = 1/1; Refinement method: Full-matrix least-squares on F^2.

Compound	DCPFA	DCPMA	DCPDMA	DCPTMA
Chemical formula	$C_7H_5Cl_2NO$	$C_9H_9Cl_2NO$	$C_{10}H_{11}Cl_2NO$	$C_{11}H_{13}Cl_2NO$
Formula weight	190.02	218.07	232.10	246.12
Temperature, K	297(2)	297(2)	296(2)	297(2)
Wavelength, pm	71.073	71.073	71.073	71.069
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	Pbca	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a, Å	8.593(3)	4.774(2)	9.901(4)	16.047(5)
b, Å	12.728(4)	10.961(5)	13.785(5)	9.882(3)
c, Å	14.376(4)	19.562(8)	9.060(3)	16.270(5)
β, deg.	90	90	103.58(2)	102.12 (1)
Volume, Å^3	1572.3(9)	1023.6(8)	1202.0(8)	2522.5(13)
Z	8	4	4	8
D_{calcd}, g·cm^{-3}	1.605	1.415	1.283	1.296
Abs. coeff., cm^{-1}	7.59	5.93	5.09	0.489
F(000)	768	448	480	1024
Crystal size, mm^3	2.50×0.50×0.24	2.0×0.24×0.21	2.30×0.30×0.15	0.75×0.32×0.25
θ range, deg.	2.83 to 27.50 deg.	2.08 to 27.47	2.12 to 27.47	1.62 to 22.51
Index ranges	$0 \leq h \leq 11, -16 \leq k \leq 7, -18 \leq l \leq 18$	$0 \leq h \leq 6, -14 \leq k \leq 3, -25 \leq l \leq 25$	$-12 \leq h \leq 12, -17 \leq k \leq 3, 0 \leq l \leq 11$	$-14 \leq h \leq 17, -10 \leq k \leq 0, -17 \leq l \leq 17$
Reflections coll.	5499	3483	3609	6405
Independent refl.	1806	2353	2747	3309
[*R*(int)]	0.0212	0.0140	0.0217	0.0127
Absorption corr.	numeric	numeric	numeric	numeric
Max. and min. transm.	0.849, 0.690	0.926, 0.843	0.936, 0.872	0.919, 0.849
Data	1806	2353	2741	3305
Restraints/parameters	0 / 104	0 / 123	0 / 133	0 / 284
Goodness-of-fit on F^2	1.072	1.043	1.026	1.058
Final $R[I > 2\sigma(I)]$	$R1 = 0.0452$	$R1 = 0.0438$	$R1 = 0.0638$	$R1 = 0.0443$
	$wR2 = 0.1265$	$wR2 = 0.1117$	$wR2 = 0.1615$	$wR2 = 0.1105$
R indices (all data)	$R1 = 0.0512$	$R1 = 0.0573$	$R1 = 0.1011$	$R1 = 0.0567$
	$wR2 = 0.1363$	$wR2 = 0.1266$	$wR2 = 0.2115$	$wR2 = 0.1241$
Abs. Str. parameter	–	–0.05(11)	–	–
Extinction coeff.	0.025(3)	0.038(4)	0.057(6)	0.0026(6)
Largest diff. Peak and hole e$^-$ Å^3	0.373 and –0.378	0.167 and –0.234	0.230 and –0.255	0.349 and –0.369

the compounds, N-(2,6-dichlorophenyl)-formamide, 2,6-$Cl_2C_6H_3$-NHCO-H (**DCPFA**); N-(2,6-dichlorophenyl)-2-methylacetamide (propionamide), 2,6-$Cl_2C_6H_3$-NHCO-CH_2CH_3 (**DCPMA**); N-(2,6-dichlorophenyl)-2,2-dimethylacetamide (isobutylamide or 2-methylpropionamide), 2,6-$Cl_2C_6H_3$-NHCO-$CH(CH_3)_2$ (**DCPDMA**) and N-(2,6-dichlorophenyl)-2,2,2-trimethylacetamide (neopentylamide or pivalic acid amide or 2,2-dimethylpropionamide), 2,6-$Cl_2C_6H_3$-NHCO-$C(CH_3)_3$ (**DCPTMA**). Further, we have analysed the present data along with the ^{35}Cl NQR spectra and / or the crystal structures of 2,6-dichloroaniline, 2,6-$Cl_2C_6H_3$-NH_2 (**DCA**) [19, 20], N-(2,6-dichlorophenyl)-acetamide, 2,6-$Cl_2C_6H_3$-NHCO-CH_3 (**DCPA**), N-(2,6-dichlorophenyl)-2-chloroacetamide, 2,6-$Cl_2C_6H_3$-NHCO-CH_2Cl (**DCPCA**), N-(2,6-dichlorophenyl)-2,2-dichloroacetamide, 2,6-$Cl_2C_6H_3$-NHCO-$CHCl_2$ (**DCPDCA**), N-(2,6-dichlorophenyl)-2,2,2-trichloroacetamide, 2,6-$Cl_2C_6H_3$-NHCO-CCl_3 (**DCPTCA**) [17]; N-(phenyl)-acetamide, C_6H_5-NHCO-CH_3 (**PA**) [21] and N-(phenyl)-2,2,2-trichloroacetamide, C_6H_5-NHCO-CCl_3 (**PTCA**) [7], in an effort to know the overall effect of side chain substitution on the ^{35}Cl NQR ring C-Cl frequencies and crystal structures of amides of the type, N-(2,6-dichlorophenyl)-amides,

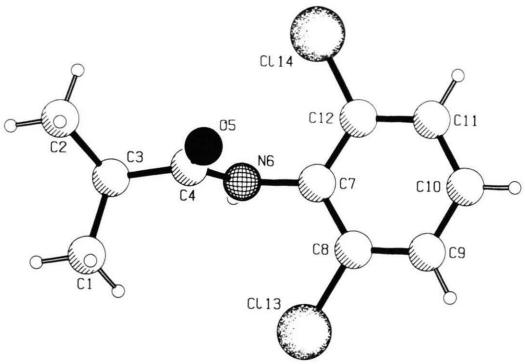

Fig. 3. Molecular geometry of N-(2,6-dichlorophenyl)-2,2-dimethylacetamide, 2,6-$Cl_2C_6H_3$-NHCO-$CH(CH_3)_2$ (**DCPDMA**), with the numbering of atoms.

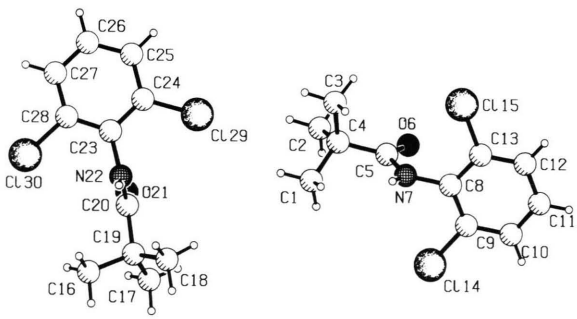

Fig. 4. Molecular geometry of N-(2,6-dichlorophenyl)-2,2,2-trimethylacetamide, 2,6-$Cl_2C_6H_3$-NHCO-$C(CH_3)_3$ (**DCPTMA**), with the numbering of atoms.

2,6-$Cl_2C_6H_3$-NHCO-R (R = H, $CH_{3-y}X_y$ where X = CH_3 or Cl and y = 0, 1, 2 or 3).

Experimental

Preparation and Characterisation of the Compounds

The commercial 2,6-dichloroaniline was purified by zone refining. The liquids were purified by double distillations. The compound **DCPFA** was prepared by treating 2,6-dichloroaniline with a clear mixture of formic acid with phosphoryl chloride (Aldrich, Germany) under constant stirring. The mixture was slowly warmed to expel HCl. Excess phosphoryl chloride was hydrolysed by adding cold water dropwise under ice cold conditions. The solid was filtered under suction, washed thoroughly with water and dried. The compounds **DCPMA, DCPDMA** and **DCPTMA** were prepared, respectively, from 2,6-dichloroaniline and propionyl chloride; 2,6-dichloroaniline and isobutyric acid chloride (2-methylpropionylchloride); 2,6-dichloroaniline and pivaloyl chloride (2,2,2-trimethyl-acetylchloride) in benzene or acetone [6, 16, 22]. The compounds were recrystallised from ethanol several times. The purity of the compounds was checked by elemental analysis (C, H and N): % (found/calculated) – **DCPFA:** C (44.02 / 44.24), H (2.60 / 2.65) and N (7.37 / 7.48); **DCPMA:** C (49.45 / 49.57), H (4.11 / 4.16) and N (6.45 / 6.42); **DCPDMA:** C (49.95 / 51.47), H (4.69

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{ij}
2,6-$Cl_2C_6H_3$-NHCO-H (DCPFA)				
O(1)	1316(2)	1649(2)	3265(1)	61(1)
C(2)	–14(2)	1610(2)	2987(1)	45(1)
N(3)	–486(2)	1227(2)	2170(1)	40(1)
C(4)	545(2)	833(2)	1491(1)	37(1)
C(5)	698(2)	1334(2)	631(1)	42(1)
C(6)	1667(2)	945(2)	–58(2)	51(1)
C(7)	2528(3)	52(2)	115(2)	60(1)
C(8)	2410(3)	–462(2)	956(2)	56(1)
C(9)	1405(2)	–81(2)	1629(2)	44(1)
Cl(10)	–380(1)	2455(1)	414(1)	54(1)
Cl(11)	1180(1)	–792(1)	2649(1)	66(1)
2,6-$Cl_2C_6H_3$-NHCO-CH_2CH_3 (DCPMA)				
C(1)	4603(9)	1245(3)	989(2)	84(1)
C(2)	2731(6)	2304(3)	903(2)	72(1)
C(3)	4038(5)	3512(2)	1085(2)	53(1)
O(4)	6548(4)	3626(2)	1174(1)	69(1)
N(5)	2243(4)	4454(2)	1141(1)	56(1)
C(6)	3083(5)	5646(2)	1336(1)	53(1)
C(7)	2174(6)	6136(2)	1953(2)	58(1)
C(8)	2969(7)	7287(3)	2168(2)	71(1)
C(9)	4730(9)	7952(3)	1766(2)	85(1)
C(10)	5693(8)	7509(3)	1149(2)	83(1)
C(11)	4820(7)	6351(3)	935(2)	65(1)
Cl(12)	–22(2)	5289(1)	2474(1)	78(1)
Cl(13)	5905(2)	5842(1)	147(1)	99(1)
2,6-$Cl_2C_6H_3$-NHCO-$CH(CH_3)_2$ (DCPDMA)				
C(1)	97(5)	3235(5)	–1687(7)	136(2)
C(2)	1639(6)	4683(3)	–945(5)	108(2)
C(3)	1562(4)	3621(3)	–1387(4)	78(1)
C(4)	2473(3)	3010(2)	–159(3)	63(1)
O(5)	2578(3)	3173(2)	1190(2)	79(1)
N(6)	3130(3)	2265(2)	–643(3)	66(1)
C(7)	3864(3)	1563(2)	358(3)	61(1)
C(8)	3278(4)	666(3)	533(4)	71(1)
C(9)	3987(5)	–38(3)	1492(4)	84(1)
C(10)	5309(5)	157(3)	2321(4)	91(1)
C(11)	5924(4)	1037(3)	2186(4)	85(1)
C(12)	5209(4)	1730(2)	1213(4)	69(1)
Cl(13)	1604(1)	434(1)	–481(1)	105(1)
Cl(14)	6021(1)	2808(1)	994(2)	105(1)

Table 3 (continued).
2,6-$Cl_2C_6H_3$-NHCO-$C(CH_3)_3$ (DCPTMA).

Atom	x	y	z	U_{ij}
C(1)	4096(3)	1143(5)	2497(3)	108(2)
C(2)	4357(2)	–941(4)	3366(3)	105(1)
C(3)	3862(3)	147(5)	3961(3)	117(2)
C(4)	3800(2)	301(3)	3162(2)	62(1)
C(5)	2873(2)	–136(3)	2870(2)	55(1)
O(6)	2629(1)	–1283(2)	2962(2)	73(1)
N(7)	2316(2)	827(3)	2510(2)	59(1)
C(8)	1435(2)	563(3)	2277(2)	53(1)
C(9)	1064(2)	118(3)	1478(2)	67(1)
C(10)	196(3)	–153(4)	1259(3)	85(1)
C(11)	–297(2)	43(4)	1835(3)	87(1)
C(12)	45(2)	492(4)	2622(3)	78(1)
C(13)	907(2)	739(3)	2837(2)	62(1)
Cl(14)	1690(1)	–93(1)	745(1)	108(1)
Cl(15)	1340(1)	1322(1)	3836(1)	100(1)
C(16)	7897(3)	3348(5)	1060(2)	100(1)
C(17)	6965(3)	1320(4)	754(2)	92(1)
C(18)	6399(2)	3439(4)	1242(2)	85(1)
C(19)	7183(2)	2547(3)	1320(2)	57(1)
C(20)	7503(2)	2082(3)	2219(2)	52(1)
O(21)	7706(2)	911(2)	2406(1)	73(1)
N(22)	7586(2)	3034(2)	2825(2)	58(1)
C(23)	7959(2)	2750(3)	3674(2)	54(1)
C(24)	7487(2)	2232(3)	4223(2)	64(1)
C(25)	7871(3)	1967(4)	5059(2)	88(1)
C(26)	8727(4)	2226(5)	5327(3)	105(2)
C(27)	9195(3)	2747(5)	4803(3)	101(1)
C(28)	8813(2)	3008(3)	3989(2)	72(1)
Cl(29)	6418(1)	1938(1)	3879(1)	97(1)
Cl(30)	9415(1)	3719(1)	3332(1)	109(1)

/ 4.79) and N (5.89 / 6.07); **DCPTMA:** C (53.49 / 53.68), H (5.33 / 5.32) and N (5.70 / 5.69) and by determining their melting points – **DCPFA** (178 °C), **DCPMA** (152 - 153 °C) and**DCPDMA** (147 °C). The compounds, **DCPFA**, **DCPMA**, **DCPDMA**, and **DCPTMA** were further characterised by recording their infrared spectra. All other reagents employed in the preparations and purification of compounds were of analytical grade.

^{35}Cl NQR Spectral Studies

Polycrystalline samples of the title compounds were employed. The ^{35}Cl NQR of the compounds, **DCPFA**, **DCPMA**, **DCPDMA** and **DCPTMA** were measured at 77 K with a Decca NQR spectrometer. The spectra were registered by the continuous wave method with a superregenerative spectrometer. The temperature at the sample site was produced by a stream of temperature and flow regulated nitrogen gas

Table 4. Bond lengths (Å) (standard deviation).

Connection	Bond length	Connection	Bond length
DCPFA		DCPA	
O(1)-C(2)	1.212(3)	C(2)-C(1)	1.498(3)
C(2)-N(3)	1.335(3)	C(2)-O(3)	1.228(3)
N(3)-C(4)	1.410(2)	C(2)-N(4)	1.346(3)
C(4)-C(9)	1.392(3)	N(4)-C(5)	1.414(3)
C(4)-C(5)	1.397(3)	C(5)-C(10)	1.389(4)
C(5)-C(6)	1.386(3)	C(5)-C(6)	1.388(4)
C(6)-C(7)	1.379(4)	C(6)-C(7)	1.384(4)
C(7)-C(8)	1.378(4)	C(7)-C(8)	1.367(5)
C(8)-C(9)	1.385(3)	C(8)-C(9)	1.375(5)
C(5)-Cl(10)	1.730(2)	C(9)-C(10)	1.378(4)
C(9)-Cl(11)	1.734(2)	C(6)-Cl(11)	1.732(3)
		C(10)-Cl(12)	1.728(3)
DCPMA		DCPDMA	
C(1)-C(2)	1.474(5)	C(1)-C(3)	1.509(7)
C(2)-C(3)	1.507(4)	C (2)-C(3)	1.515(6)
C(3)-O(4)	1.217(3)	C(3)-C(4)	1.512(4)
C(3)-N(5)	1.347(3)	C(4)-O(5)	1.223(3)
N(5)-C(6)	1.419(3)	C(4)-N(6)	1.344(4)
C(6)-C(11)	1.378(4)	N(6)-C(7)	1.406(4)
C(6)-C(7)	1.390(4)	C(7)-C(12)	1.393(4)
C(7)-C(8)	1.384(4)	C(7)-C(8)	1.391(5)
C(8)-C(9)	1.362(5)	C(8)-C(9)	1.380(5)
C(9)-C(10)	1.381(5)	C(9)-C(10)	1.374(6)
C(10)-C(11)	1.400(5)	C(10)-C(11)	1.375(6)
C(7)-Cl(12)	1.732(3)	C(11)-C(12)	1.378(5)
C(11)-Cl(13)	1.720(3)	C(8)-Cl(13)	1.726(4)
		C(12)-Cl(14)	1.723(4)
	— DCPTMA —		
C(1)-C(4)	1.519(5)	C(16)-C(19)	1.524(5)
C (2)-C(4)	1.514(5)	C (17)-C(19)	1.518(4)
C(3)-C(4)	1.531(5)	C(18)-C(19)	1.520(5)
C(4)-C(5)	1.526(4)	C(19)-C(20)	1.516(4)
C(5)-O(6)	1.219(4)	C(20)-O(21)	1.223(3)
C(5)-N(7)	1.352(4)	C(20)-N(22)	1.349(4)
N(7)-C(8)	1.409(4)	N(22)-C(23)	1.413(4)
C(8)-C(13)	1.379(4)	C(23)-C(28)	1.381(5)
C(8)-C(9)	1.382(4)	C(23)-C(24)	1.384(4)
C(9)-C(10)	1.391(5)	C(24)-C(25)	1.396(5)
C(10)-C(11)	1.361(6)	C(25)-C(26)	1.374(6)
C(11)-C(12)	1.357(5)	C(26)-C(27)	1.350(6)
C(12)-C(13)	1.377(5)	C(27)-C(28)	1.363(5)
C(9)-Cl(14)	1.725(4)	C(24)-Cl(29)	1.714(4)
C(13)-Cl(15)	1.727(3)	C(28)-Cl(30)	1.734(4)

or with a liquid nitrogen bath at 77 K. The temperatures at the sample site were measured by copper-constantan thermocouples to ±1 K. The resonance frequencies were measured via a frequency counter to an accuracy of ±5 kHz. The latter accuracy was determined by the line width of the resonances, which was between 10 and 20 kHz.

The compounds **DCA**, **DCPA**, **DCPCA**, **DCPDCA**, **DCPTCA**, and **PTCA** were also ob-

Table 5. Bond angles (degree) (standard deviation).

Connection	Bond angle	Connection	Bond angle
DCPFA		DCPA	
O(1)-C(2)-N(3)	126.3(2)	O(3)-C(2)-C(1)	122.2(3)
C(2)-N(3)-C(4)	123.2(2)	O(3)-C(2)-N(4)	123.0(2)
C(9)-C(4)-C(5)	117.2(2)	N(4)-C(2)-C(1)	114.8(2)
C(9)-C(4)-N(3)	122.1(2)	C(2)-N(4)-C(5)	123.1(3)
C(5)-C(4)-N(3)	120.6(2)	C(10)-C(5)-C(6)	117.2(3)
C(6)-C(5)-C(4)	121.8(2)	C(10)-C(5)-N(4)	121.8(3)
C(7)-C(6)-C(5)	119.2(2)	C(6)-C(5)-N(4)	121.0(3)
C(8)-C(7)-C(6)	120.7(2)	C(7)-C(6)-C(5)	121.7(3)
C(7)-C(8)-C(9)	119.5(2)	C(8)-C(7)-C(6)	119.2(4)
C(8)-C(9)-C(4)	121.6(2)	C(7)-C(8)-C(9)	121.1(4)
C(6)-C(5)-Cl(10)	119.1(2)	C(8)-C(9)-C(10)	119.0(3)
C(4)-C(5)-Cl(10)	119.1(2)	C(5)-C(10)-C(9)	121.9(3)
C(8)-C(9)-Cl(11)	118.6(2)	C(5)-C(6)-Cl(11)	118.9(2)
C(4)-C(9)-Cl(11)	119.8(2)	C(7)-C(6)-Cl(11)	119.4(3)
		C(5)-C(10)-Cl(12)	119.7(2)
		C(9)-C(10)-Cl(12)	118.3(2)
DCPMA		DCPDMA	
C(1)-C(2)-C(3)	114.4(3)	C(1)-C(3)-C(4)	108.6(3)
O(4)-C(3)-N(5)	122.4(3)	C(1)-C(3)-C(2)	112.0(4)
O(4)-C(3)-C(2)	122.1(3)	C(4)-C(3)-C(2)	111.0(3)
N(5)-C(3)-C(2)	115.4(2)	O(5)-C(4)-N(6)	122.2(3)
C(3)-N(5)-C(6)	123.2(2)	O(5)-C(4)-C(3)	121.9(3)
C(11)-C(6)-C(7)	117.8(3)	N(6)-C(4)-C(3)	115.9(3)
C(11)-C(6)-N(5)	122.2(3)	C(4)-N(6)-C(7)	122.1(2)
C(7)-C(6)-N(5)	120.0(2)	C(8)-C(7)-C(12)	116.9(3)
C(8)-C(7)-C(6)	122.0(3)	C(8)-C(7)-N(6)	121.3(3)
C(9)-C(8)-C(7)	118.8(3)	C(12)-C(7)-N(6)	121.8(3)
C(8)-C(9)-C(10)	121.5(3)	C(9)-C(8)-C(7)	122.3(3)
C(9)-C(10)-C(11)	118.8(3)	C(10)-C(9)-C(8)	119.0(4)
C(6)-C(11)-C(10)	121.2(3)	C(9)-C(10)-C(11)	120.6(4)
C(8)-C(7)-Cl(12)	118.4(3)	C(10)-C(11)-C(12)	119.8(4)
C(6)-C(7)-Cl(12)	119.6(2)	C(11)-C(12)-C(7)	121.4(4)
C(6)-C(11)-Cl(13)	120.6(2)	C(9)-C(8)-Cl(13)	119.2(3)
C(10)-C(11)-Cl(13)	118.2(3)	C(7)-C(8)-Cl(13)	118.6(3)
		C(11)-C(12)-Cl(14)	119.2(3)
		C(7)-C(12)-Cl(14)	119.3(3)

tained/prepared, characterised and their ^{35}Cl NQR frequencies were measured under identical conditions for comparison purposes.

Crystal Structure Studies

Small single crystals of **DCPFA**, **DCPMA**, **DCPDMA** and **DCPTMA** were selected for X-ray diffraction and studied at room temperature. The collected intensity data were corrected for Lorentz polarisation and absorption. The positional parameters were determined by direct methods and least squares refinement (SHELXL-93) [23 - 28]. For locating the hydrogen atom positions, the C-H distances were fixed to 0.93 Å for the ring hydrogen atoms, while

Table 5 (continued). DCPTMA.

Connection	Bond angle	Connection	Bond angle
C(2)-C(4)-C(1)	110.0(3)	C(20)-C(19)-C(17)	109.3(3)
C(2)-C(4)-C(5)	109.3(3)	C(20)-C(19)-C(18)	111.3(3)
C(1)-C(4)-C(5)	111.3(3)	C(17)-C(19)-C(18)	109.4(3)
C(2)-C(4)-C(3)	109.1(3)	C(20)-C(19)-C(16)	107.6(3)
C(1)-C(4)-C(3)	109.4(3)	C(17)-C(19)-C(16)	109.8(3)
C(5)-C(4)-C(3))	107.7(3)	C(18)-C(19)-C(16)	109.5(3)
O(6)-C(5)-N(7)	120.5(3)	O(21)-C(20)-N(22)	119.8(3)
O(6)-C(5)-C(4)	122.9(3)	O(21)-C(20)-C(19)	123.0(3)
N(7)-C(5)-C(4)	116.6(3)	N(22)-C(20)-C(19)	117.1(2)
C(5)-N(7)-C(8)	121.4(3)	C(20)-N(22)-C(23)	122.2(2)
C(13)-C(8)-C(9)	117.3(3)	C(28)-C(23)-C(24)	117.6(3)
C(13)-C(8)-N(7)	121.3(3)	C(28)-C(23)-N(22)	120.6(3)
C(9)-C(8)-N(7)	121.4(3)	C(24)-C(23)-N(22)	121.8(3)
C(8)-C(9)-C(10))	120.9(3)	C(23)-C(24)-C(25)	120.6(4)
C(8)-C(9)-Cl(14)	119.4(3)	C(23)-C(24)-Cl(29)	119.9(3)
C(10)-C(9)-Cl(14)	119.7(3)	C(25)-C(24)-Cl(29)	119.6(3)
C(11)-C(10)-C(9)	119.4(4)	C(26)-C(25)-C(24)	118.8(4)
C(12)-C(11)-C(10)	121.2(4)	C(27)-C(26)-C(25)	121.4(4)
C(11)-C(12)-C(13)	118.9(4)	C(26)-C(27)-C(28)	119.3(4)
C(12)-C(13)-C(8)	122.3(3)	C(27)-C(28)-C(23)	122.3(4)
C(12)-C(13)-Cl(15)	118.9(3)	C(27)-C(28)-Cl(30)	118.8(3)
C(8)-C(13)-Cl(15)	118.9(2)	C(23)-C(28)-Cl(30)	119.0(3)

the side chain C-H distances were fixed to 0.96 Å for the CH_3 group. Further experimental conditions for structure determinations and refinements are given in Table 1.

Results and Discussion

^{35}Cl (ω) NQR frequencies of the compounds **DCPFA**, **DCPMA**, **DCPDMA** and **DCPTMA** alongwith those of **DCA**, **DCPA**, **DCPCA**, **DCPDCA**, and **DCPTCA** are shown in Table 1. There was no problem in assigning the frequencies as there are only ring C-Cl ^{35}Cl NQR frequencies in all the four copounds **DCPFA**, **DCPMA**, **DCPDMA** and **DCPTMA**. All the substituted amides and **DCA** (Table 1), except **DCPDMA** and **DCPTMA**, showed two ^{35}Cl ring C-Cl frequencies for the two chlorine atoms present in them. The **DCPDMA** showed only one ring C-Cl NQR frequency at 35.775 MHz, which may be due to the crystallographical equivalence of the 2 Cl atoms in it, while the **DCPTMA** showed 4 ring C-Cl ^{35}Cl NQR frequencies for the 2 Cl atoms present in it, indicating that there may be two molecules in it's asymmetric unit. This was confirmed by the crystal structure results on the compound (Tables 3 - 5). Further, the ring ^{35}Cl$^{(2,6)}$ NQR frequencies in the substituted amides generally decreased with increase in electron donating groups (CH_3) in the side chain and increased with

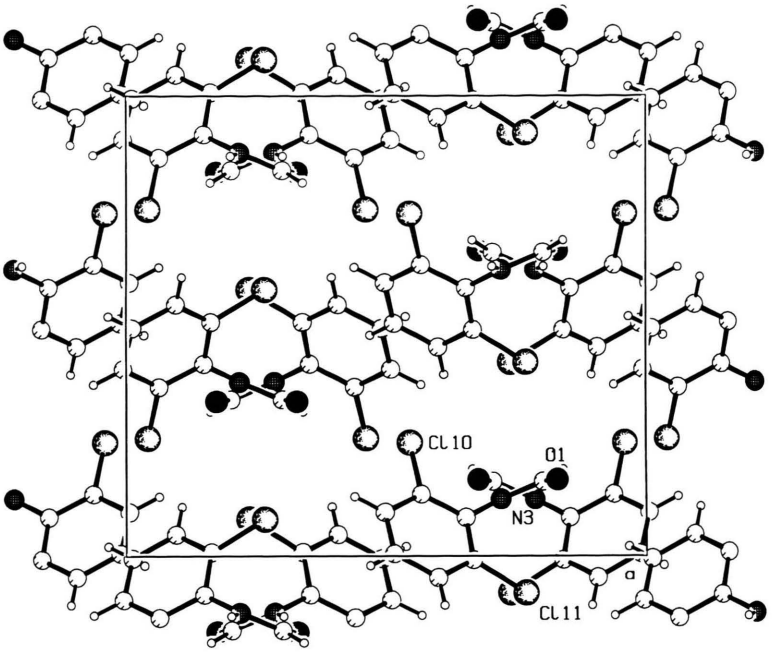

Fig. 5. Projection of the unit cell of **DCPFA** along [100] on to the *bc* plane.

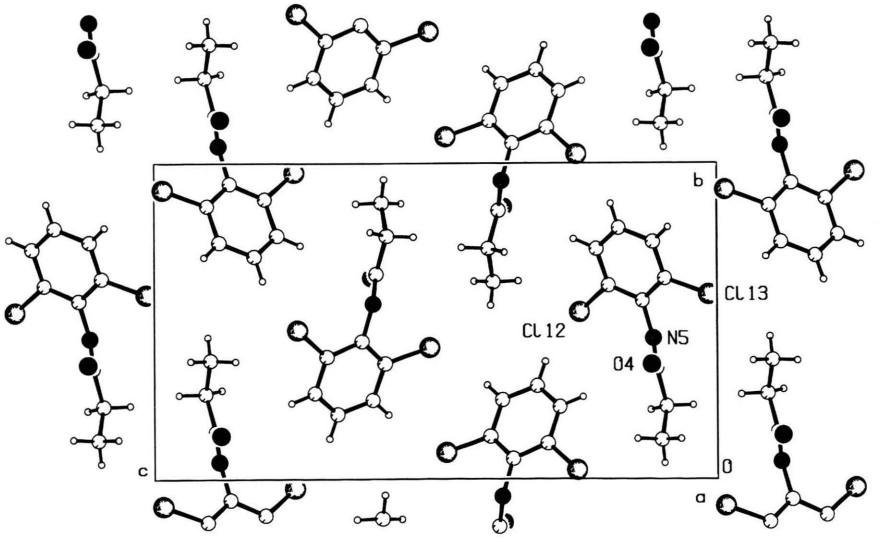

Fig. 6. Projection of the unit cell of **DCPMA** along [100] on to the *bc* plane.

increase in electron withdrawing atoms (Cl) in the side chain (Table 1). The changes in frequencies are marginal as the effects are to be transmitted through the peptide linkage.

The crystallographic data for the compounds, **DCPFA**, **DCPMA**, **DCPDMA** and **DCPTMA** are given in Table 2. The atomic coordinates and the mean displacement parameters are listed in Table 3, while Tables 4 and 5 give the intramolecular bond distances and bond angles, respectively. The latter tables also contain the bond distances and bond angles for the side chain unsubstituted compound **DCPA**. The hydrogen coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations have been deposited at the Cambridge Crystallographic Data Centre, the CCDC numbers are 148982 - 148985. Figures 1 - 4 show the molecules of the compounds, **DCPFA**, **DCPMA**, **DCPDMA** and **DCPTMA** as they appear in suitable projection with the numbering of the atoms used throughout the paper.

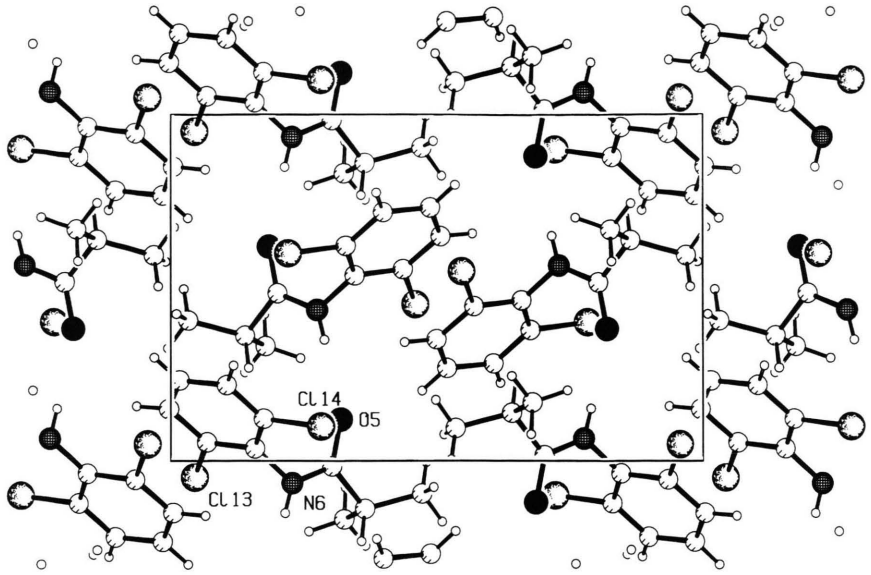

Fig. 7. Projection of the unit cell of **DCPDMA** along [100].

The projections of the unit cells of the compounds, **DCPFA**, **DCPMA**, **DCPDMA** and **DCPTMA** are shown in Figures 5 - 8.

We shall discuss the present crystal structure data on the compounds **DCPFA**, **DCPMA**, **DCPDMA** and **DCPTMA** along with those of **DCA**, **DCPA**, **DCPCA**, **DCPTCA**, **PTCA** and **PA**. N-(2,6-dichlorophenyl)-amine or 2,6-dichloroaniline (**DCA**) crystallises in the monoclinic crystal symmetry. The conversion of **DCA** (monoclinic) into various acid amides **DCPFA** (orthorhombic), **DCPA** (monoclinic), **DCPMA** (orthorhombic), **DCPDMA** (monoclinic), **DCPTMA** (monoclinic), **DCPCA** (orthorhombic) and **DCPTCA** (monoclinic) affects it's crystal symmetry. Let us discuss the effect using **DCPA** as reference, which also crystallises in the monoclinic crystal system. The replacement of the side chain CH_3 group by the H atom or substitution of either a CH_3 group or a Cl atom for one of the H atoms in the side chain CH_3 group or replacement of the two ring Cl atoms by the H atoms changes the crystal symmetry from monoclinic to orthorhombic, while the substitution of 2 or all the 3 H atoms in the CH_3 group of **DCPA** by 2 or 3 CH_3 groups or Cl atoms restores it's crystal symmetry back to the monoclinic type. Similarly the conversion of **PA** into either **DCPA** or **PTCA** by introducing 2 Cl atoms into the phenyl ring at 2nd and 6th positions or replacing all the 3 H atoms by the Cl atoms, respectively, changes the crystal symmetry from orthorhombic to monoclinic. These are only the observations based on the available data. Before generalising these observations, an extensive work needs to be carried out with change of both the substituent and the site of substitution in the phenyl ring under varying side chain substitutions. Work in this direction is in progress in our group.

We will now turn to the intramolecular geometry of the four title compounds **DCPFA**, **DCPMA**, **DCPDMA**, and **DCPTMA** in comparison with the compounds, **DCA**, **DCPA**, **DCPCA**, and **DCPTCA**. The range of C(i)-C(j) bond distances within the phenyl rings of the compounds does not show significant changes with the substitution of either the electron donating or the electron withdrawing groups at the side chain. The observed mean ring distances for the compounds are as follows. The minimum and maximum bond lengths in Å are given in parentheses.:1.375 (1.362, 1.392); 1.386 (1.379, 1.397); 1.380 (1.367, 1.389); 1.383 (1.362, 1.400); 1.382 (1.374, 1.393); 1.375 (1.350, 1.396); 1.383 (1.370, 1.390) and 1.380 (1.373, 1.390) Å for the compounds, **DCA**, **DCPFA**, **DCPA**, **DCPMA**, **DCPDMA**, **DCPTMA**, **DCPCA**, and **DCPTCA**, respectively. As may be seen, the mean distances of all the compounds lie in the range 1.375 - 1.386 Å, the minimum mean value is for the **DCA** and **DCPTMA** and the maximum mean value is for the **DCPFA**. The range of the six ring distances is wider (1.350 - 1.396 Å) for the compound **DCPTMA** and narrower with **DCPFA** (1.379 - 1.397 Å). The C(ring)-Cl mean distances for the compounds **DCA**, **DCPFA**, **DCPA**, **DCPMA**, **DCPDMA**, **DCPTMA**, **DCPCA**,

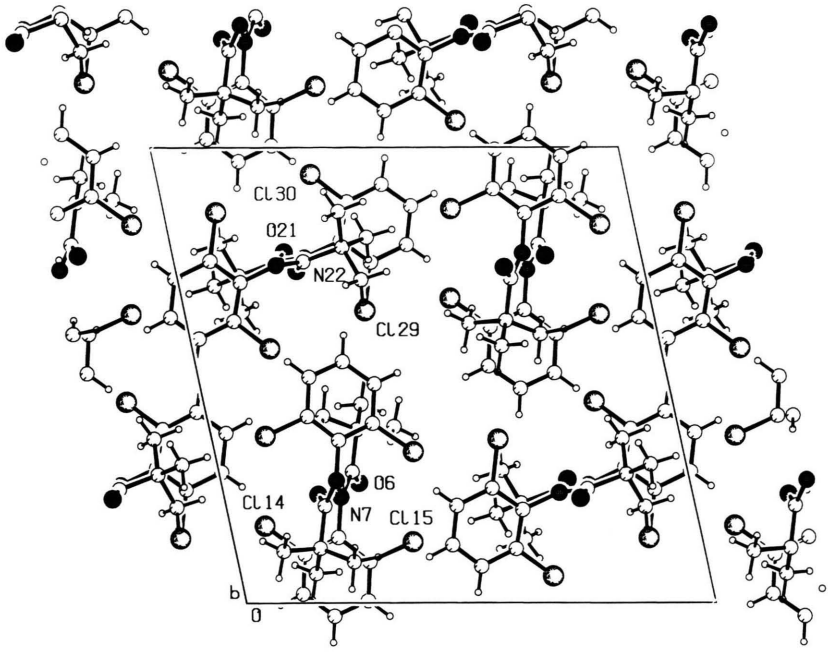

Fig. 8. Projection of the unit cell of **DCPTMA** along [010] on to the *ac* plane.

and **DCPTCA** are 1.738, 1.732, 1.730, 1.726, 1.724, 1.725, 1.729 and 1.722 Å, respectively. This mean distance of **DCA** decreases slightly on converting it into the substituted amides. The C(ring)-N distances for the compounds **DCA**, **DCPFA**, **DCPA**, **DCPMA**, **DCPDMA**, **DCPTMA**, **DCPCA**, and **DCPTCA** are 1.371, 1.410, 1.414, 1.419, 1.406, 1.411, 1.416 and 1.429 Å, respectively. This distance increases on transforming N-(2,6-dichlorophenyl)-amine into it's substituted amides as above and is maximum for the compound **DCPTCA**, in which the side chain contains 3 electron withdrawing Cl atoms. The C(O)-N bond distances are 1.335, 1.346, 1.346, 1.347, 1.344, 1.351, 1.336 and 1.336 Å for the compounds,**DCPFA**, **DCPA**, **DCPMA**, **DCPDMA**, **DCPTMA**, **DCPCA**, and **DCPTCA**, respectively. This distance is slightly longer for the compounds with electron donating groups in the side chain and shorter for the compounds with electron withdrawing groups in the side chain. The C-O bond length lies in the range 1.210 - 1.223 Å, the minimum and maximum values are for **DCPTCA** and **DCPDMA**, respectively. It is slightly shortened with the replacement of the 3 H atoms in the side chain -CH_3 group by the electron withdrawing Cl atoms. The C(O)-C(side) bond lengths show similar trends with the values being 1.498, 1.507, 1.512, 1.521, 1.525 and 1.550 Å for **DCPA**, **DCPMA**, **DCPDMA**, **DCPTMA**, **DCPCA**, and **DCPTCA**, respectively, which increases on substitution of the electron withdrawing Cl atoms in the side chain.

If we now turn to the bond angles, they are observed between the ranges listed as follows: 115.6° and 123.2° (**DCA**), 117.2° and 121.8° (**DCPFA**), 117.2° and 121.9° (**DCPA**), 117.8° and 122.0° (**DCPMA**), 116.9° and 122.3° (**DCPDMA**), 117.3° and 122.3° (**DCPTMA**), 117.8° and 122.1° (**DCPCA**) and 118.7° and 121.7° (**DCPTCA**). The deviations of the individual values from 120° are maximum for **DCA** and minimum for **DCPTCA**. C2(ring)-C1(ring)-N and C6(ring)-C1(ring)-N angles for the compounds are 122.1° and 122.2° (**DCA**), 120.6° and 122.1° (**DCPFA**), 121.0° and 121.8° (**DCPA**), 120.0° and 122.2° (**DCPMA**), 121.3° and 121.8° (**DCPDMA**), 120.6° and 121.8° (**DCPTMA**), 120.3° and 121.9° (**DCPCA**) and 120.6° and 120.6° (**DCPTCA**). The deviations of these angles from 120° are minimum for **DCPTCA** and maximum for **DCA**. The C2(ring)-C1(ring)-C6(ring) bond angles also show similar trends with the values being 115.6°, 117.2°, 117.2°, 117.8°, 116.9° , 117.5°, 117.8° and 118.8° for the compounds, **DCA**, **DCPFA**, **DCPA**, **DCPMA**, **DCPDMA**, **DCPTMA**, **DCPCA** and **DCPTCA**, respectively. The C(ring)-N-C(O) bond angles vary as 123.2° (**DCPFA**), 123.1° (**DCPA**), 123.2° (**DCPMA**), 122.1° (**DCPDMA**),

121.8° (**DCPTMA**), 123.4° (**DCPCA**) and 121.4° (**DCPTCA**), while the N-C(O)-C(side chain) angles are 114.8° (**DCPA**), 115.4° (**DCPMA**), 115.9° (**DCPDMA**), 116.9° (**DCPTMA**), 113.5° (**DCPCA**) and 114.8° (**DCPTCA**), respectively. Similarly the O-C(O)-C(side chain) angles vary as 122.2° (**DCPA**), 122.1° (**DCPMA**), 121.9° (**DCPDMA**), 123.0° (**DCPTMA**), 122.3° (**DCPCA**) and 120.6° (**DCPTCA**), while the O-C(O)-N angles for the compounds are 126.3° (**DCPFA**), 123.0° (**DCPA**), 122.4° (**DCPMA**), 122.2° (**DCPDMA**), 120.2° (**DCPTMA**), 124.3° (**DCPCA**) and 124.6° (**DCPTCA**). The deviations of the latter angles show a trend with the substitution of the CH_3 groups for the H-atoms in the side chain CH_3, decrease with increase in the number of the CH_3 groups. Thus the deviation is minimum for **DCPTMA**.

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