Structural Studies of N-(2,4,6-trisubstitutedphenyl)-Chloroacetamides, 2,4,6-$X_3C_6H_2$-NHCO-$CH_{3-y}Cl_y$ (X = CH_3 or Cl and y = 1 - 3).

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The effect of side chain and ring substitutions on the crystal structures of N-(2,4,6-substituted-phenyl)-chloroacetamides of the type, 2,4,6-$X_3C_6H_2$-NHCO-$CH_{3-y}Cl_y$ (X = CH_3 or Cl and $1 \leq y \leq 3$), has been studied by determining the crystal structures of N-(2,4,6-trimethylphenyl)-2-chloroacetamide, 2,4,6-$(CH_3)_3C_6H_2$-NHCO-CH_2Cl (**TMPMCA**); N-(2,4,6-trichlorophenyl)-2-chloroacetamide, 2,4,6-$Cl_3C_6H_2$-NHCO-CH_2Cl (**TCPMCA**); N-(2,4,6-trichlorophenyl)-2,2-dichloroacetamide, 2,4,6-$Cl_3C_6H_2$-NHCO-$CHCl_2$ (**TCPDCA**) and N-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide, 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (**TCPTCA**). The crystal type, space group, formula units and lattice constants in Å are: (**TMPMCA**); monoclinic, $P2_1/n$, $Z = 8$, $a = 9.029(5)$, $b = 15.688(2)$, $c = 16.150(3)$, $\beta = 96.77(2)°$; (**TCPMCA**): orthorhombic, $Pna2_1$, $Z = 8$, $a = 30.708(4)$, $b = 4.685(1)$, $c = 14.506(2)$; (**TCPDCA**) orthorhombic, $P2_12_12$, $Z = 4$, $a = 16.459(3)$, $b = 15.240(3)$, $c = 4.640(1)$ and (**TCPTCA**): triclinic, $P\bar{1}$, $Z = 4$, $a = 9.828(2)$, $b = 11.953(2)$, $c = 12.278(2)$, $\alpha = 71.05(1)°$, $\beta = 75.26(2)°$, $\gamma = 83.29(1)°$. The results have been analysed along with the structures of the ring unsubstituted N-phenylacetamide (**PA**), N-phenyl-2,2,2-trichloro-acetamide, side chain unsubstituted N-(2,4,6-trichlorophenyl)-acetamide, 2,4,6-$Cl_3C_6H_2$-NHCO-CH_3 (**TCPA**) and the corresponding di-substituted phenyl acetamides and chloroacetamides. The compounds **TMPMCA, TCPMCA** and **TCPTCA** have 2 molecules each in their asymmetric units. This is in agreement with the multiple lines observed in the ^{35}Cl NQR spectra of **TCPTCA**. Further, this compound shows disorder as indicated by the multiplicity of the C(side chain) - Cl bonds. The compound **TCPMCA** does not show ^{35}Cl NQR spectra, while the compound **TMPMCA** shows a single frequency which fades out above 200 K, indicating that it may undergo a phase transition well below room temperature. Conversion of 2,4,6-trichloroaniline into 2,4,6-trichlorophenyl acetamide and gradual replacement of H-atoms in the side chain of the latter decreases slightly the mean ring distances of the compounds, while the replacement of the 3 Cl by 3 CH_3 groups in the ring increases it's mean distance. Changes in the mean ring distances are smaller as the effect has to be transmitted through the peptide linkage. The molecules in compounds **TCPDCA** and **TCPTCA** are linked in chains by -NH—O– hydrogen bonds (about 3 Å) between the amide groups of the molecules.

Key words: Crystal Structures; Trimethylphenyl-, Trichlorophenyl-chloroacetamides.

Introduction

Amides are of fundamental chemical interest because conjugation between nitrogen lone pair electrons and the carbonyl π-bond results in distinct physical and chemical properties [1]. The amide moiety is an important constituent of many biologically significant compounds [2]. Therefore an understanding of the formation, properties and reactions of amides is central to future developments in areas such as polypeptide and protein chemistry. Many amides exhibit pharmacological activity, which has further stimulated interest in their chemistry. Many acetanilides also exhibit fungicidal and herbicidal activities [3 - 5].

Nuclear quadrupole resonance and crystal structural studies give valuable information on bond

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Table 1. Experimental conditions for the crystal structure determination and crystallographic data of 2,4,6-$(CH_3)_3C_6H_2$-NHCO-CH_2Cl (**TMPMCA**); 2,4,6-$Cl_3C_6H_2$-NHCO-CH_2Cl (**TCPMCA**); 2,4,6-$Cl_3C_6H_2$-NHCO-$CHCl_2$ (**TCPDCA**), and 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (**TCPTCA**). Diffractometer: Nonius CAD 4; wavelength: 71.093 pm (MoK_α); Monochromator: Graphite (002); scan $\omega/2\theta$ = 1/1; Refinement method: Full-matrix least-squares on F^2.

Compound	TMPMCA	TCPMCA	TCPDCA	TCPTCA
Chemical formula	$C_{11}H_{14}ClNO$	$C_8H_5Cl_4NO$	$C_8H_4Cl_5NO$	$C_8H_3Cl_6NO$
Formula weight	211.71	272.94	307.38	341.82
Temperature, K	300(2)	300(2)	298(2)	298(2)
Crystal system	monoclinic	orthorhombic	orthorhombic	triclinic
Space group	$P2_1/n$	$Pna2_1$	$P2_12_12$	$P\bar{1}$
Z	8	8	4	4
a, Å	9.029(5)	30.708(4)	16.459(3)	9.828(2)
b, Å	15.688(2)	4.685(1)	15.240(3)	11.953(2)
c, Å	16.150(3)	14.506(2)	4.640(1)	12.278(2)
α, deg.	90	90	90	71.05(1)
β, deg.	96.77 (2)	90	90	75.26(2)
γ, deg.	90	90	90	83.29(1)
Volume/Å^3	2271.6(14)	2086.9(6)	1163.9(4)	1318.4(4)
D_x/(g·cm^{-3})	1.238	1.737	1.754	1.722
Abs. coeff., cm^{-1}	3.03	11.03	12.20	12.90
$F(000)$	896	1088	608	672
Crystal size/(mm)^3	0.75×0.10×0.08	0.63×0.15×0.03	0.75×0.05×0.0188	0.875×0.10×0.075
θ range, deg.	1.82 to 24.98	1.33 to 25.98	1.82 to 22.98	1.80 to 24.97
Index ranges	$-10\leq h\leq 2$, $-18\leq k\leq 0$, $-19\leq l\leq 19$	$-37\leq h\leq 37$, $-5\leq k\leq 0$, $-17\leq l\leq 0$	$-18\leq h\leq 1$, $-16\leq k\leq 1$, $-2\leq l\leq 5$	$-11\leq h\leq 1$, $-14\leq k\leq 14$, $-14\leq l\leq 14$
Refl. coll.	4847	4206	1617	5350
Independ. refl.	3991	2126	1384	4643
[R_{int}]	0.0337	0.0506	0.0756	0.0246
Data	3991	2126	1384	4642
Restraints/parameters	0 / 255	1 / 259	0 / 136	120/328
Goodness-of-fit on F^2	1.022	1.027	1.068	1.048
Final R [$I > 2\sigma(I)$]	$R1$ = 0.0632,	0.0388	0.0421	0.0977
	$wR2$ = 0.1684	0.0900	0.1027	0.3042
R (all data)	$R1$ = 0.1498,	0.0644	0.0644	0.1317
	$wR2$ = 0.2149	0.1019	0.1129	0.3557
Absol. str. parameter	0.0004(14)	0.00(11)	–0.1(2)	–
Largest diff: (peak, hole), e·Å^3	0.430, –0.304	0.369, –0.451	0.325, –0.432	1.018, –0.899

properties [6 - 9]. Thus we became interested in NQR and X-ray diffraction studies of amides in their crystalline state [10 - 18]. Pies, Rager, and Weiss [19] have studied ^{35}Cl NQR spectra of chloroacetanilides $Cl_xC_6H_{5-x}NHCOCH_{3-y}Cl_y$ and observed interesting trends in their spectra. For example, 2,4,6-$Cl_3C_6H_2$-NHCO-CH_3 (**TCPA**) and 2,4,6-$Cl_3C_6H_2$-NHCO. $CHCl_2$ (**TCPDCA**) showed 3 and 5 ^{35}Cl NQR frequencies, respectively, as expected for 3 and 5 Cl atoms present in these compounds, but 2,4,6-$Cl_3C_6H_2$-NHCO-CH_2Cl (**TCPMCA**) did not show ^{35}Cl NQR resonance, while 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (**TCPTCA**) showed multiple ^{35}Cl NQR frequencies for the 6 Cl atoms present. We have observed a single frequency for 2,4,6-$(CH_3)_3C_6H_2$-NHCO-CH_2Cl (**TCPMCA**), which fades out above 200 K [14]. There are no reports on structural studies of these compounds except for **TCPA** [20], to see how the -NHCO- bond parameters vary with substitution both in the benzene ring and in the side chain. Hence we thought it interesting to study the crystal structures of compounds of the type, 2,4,6-$X_3C_6H_2$-NHCO-CH_{3-y} Cl_y (X = CH_3 or Cl and $1 \leq y \leq 3$) and analyse the data alongwith the crystal structures of the related compounds. We report herein our results on the compounds **TMPMCA**, **TCPMCA**, **TCPDCA**, and **TCPTCA**.

Table 2. 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(eq)	Atom	x	y	z	U(eq)
2,4,6-$(CH_3)_3C_6H_2$-NHCO-CH_2Cl (TMPMCA)									
Cl(1)	10528(2)	7941(1)	402(1)	98(1)	C(2)	11264(4)	7219(3)	–229(3)	65(1)
C(3)	10105(4)	6748(3)	–809(3)	48(1)	O(4)	8766(3)	6853(2)	–775(2)	61(1)
N(5)	10651(3)	6231(2)	–1345(2)	48(1)	C(6)	9738(4)	5729(3)	–1937(3)	45(1)
C(7)	9745(4)	4844(3)	–1839(3)	51(1)	C(8)	8817(4)	4371(3)	–2419(3)	57(1)
C(9)	7928(5)	4737(3)	–3070(3)	62(1)	C(10)	8000(5)	5610(3)	–3157(3)	66(1)
C(11)	8885(4)	6125(3)	–2603(3)	55(1)	C(12)	8917(6)	7073(3)	–2721(3)	77(2)
C(13)	6924(6)	4208(4)	–3675(4)	92(2)	C(14)	10691(5)	4418(3)	–1137(3)	66(1)
Cl(15)	10466(2)	794(1)	3772(1)	93(1)	C(16)	11187(4)	–204(3)	4050(3)	67(1)
C(17)	10056(4)	–913(3)	3931(3)	49(1)	O(18)	8710(3)	–770(2)	3916(2)	68(1)
N(19)	10631(3)	–1677(2)	3865(2)	50(1)	C(20)	9790(4)	–2452(3)	3814(3)	46(1)
C(21)	9972(4)	–3019(3)	4476(3)	52(1)	C(22)	9176(5)	–3785(3)	4405(3)	64(1)
C(23)	8220(6)	–3983(3)	3705(3)	65(1)	C(24)	8051(5)	–3405(3)	3073(3)	67(1)
C(25)	8825(4)	–2630(3)	3096(3)	53(1)	C(26)	8660(6)	–2039(4)	2361(3)	75(2)
C(27)	7443(7)	–4827(4)	3615(5)	111(2)	C(28)	11015(5)	–2826(4)	5248(3)	70(1)
2,4,6-$Cl_3C_6H_2$-NHCO-$CHCl_2$ (TCPDCA)									
C(3)	10439(3)	2304(4)	5068(13)	39(2)	C(4)	9755(3)	1798(4)	6469(12)	32(1)
C(7)	8439(3)	1139(4)	5647(11)	29(1)	C(8)	8243(3)	311(4)	4682(12)	33(1)
C(9)	7551(3)	–125(4)	5586(14)	38(1)	C(10)	7055(3)	288(4)	7579(13)	40(2)
C(11)	7222(3)	1109(4)	8536(14)	37(1)	C(12)	7908(3)	1537(4)	7573(12)	32(1)
N(6)	9161(3)	1563(3)	4735(9)	31(1)	O(5)	9766(2)	1657(3)	9089(8)	48(1)
Cl(1)	11360(1)	2125(1)	6873(4)	50(1)	Cl(2)	10191(1)	3416(1)	5111(7)	88(1)
Cl(13)	8880(1)	–206(1)	2247(3)	50(1)	Cl(14)	6211(1)	–267(1)	8853(5)	65(1)
Cl(15)	8083(1)	2601(1)	8740(4)	48(1)					
2,4,6-$Cl_3C_6H_2$-NHCO-CH_2Cl (TCPMCA)									
Cl(1)	621(1)	10144(3)	–1(1)	56(1)	C(2)	234(2)	7746(10)	430(4)	45(1)
C(3)	–163(2)	9274(9)	803(4)	37(1)	O(4)	–177(2)	11853(7)	908(3)	52(1)
N(5)	–492(2)	7531(9)	1035(4)	40(1)	C(6)	–868(2)	8491(10)	1495(4)	36(1)
C(7)	–966(2)	7604(9)	2383(4)	39(1)	C(8)	–1320(2)	8564(10)	2868(4)	40(1)
C(9)	–1588(2)	10546(11)	2438(4)	43(1)	C(10)	–1516(2)	11460(12)	1555(4)	42(1)
C(11)	–1161(2)	10392(10)	1089(4)	40(1)	Cl(12)	–627(1)	5113(2)	2911(1)	51(1)
Cl(13)	–2032(1)	11893(3)	3049(1)	60(1)	Cl(14)	–1091(1)	11432(4)	–48(1)	61(1)
Cl(15)	234(1)	90(3)	3214(1)	57(1)	C(16)	639(2)	2408(11)	2832(5)	59(2)
C(17)	1016(2)	877(10)	2380(4)	40(1)	O(18)	1020(1)	–1692(6)	2269(3)	49(1)
N(19)	1341(2)	2627(8)	2119(3)	38(1)	C(20)	1707(2)	1685(9)	1621(4)	35(1)
C(21)	1800(2)	2702(9)	745(3)	35(1)	C(22)	2150(2)	1785(10)	242(4)	40(1)
C(23)	2418(2)	–232(11)	607(4)	42(1)	C(24)	2353(2)	–1263(11)	1500(4)	44(1)
C(25)	2003(2)	–268(10)	1996(4)	38(1)	Cl(26)	1451(1)	5209(3)	261(1)	47(1)
Cl(27)	2850(1)	–1563(4)	–23(1)	58(1)	Cl(28)	1947(1)	–1459(3)	3117(1)	54(1)

Experimental

Preparation and Characterisation of the Compounds

TMPMCA, **TCPMCA**, **TCPDCA** and **TCPTCA** were prepared from 2,4,6-trimethylaniline / 2,4,6-trichloroaniline and the corresponding chloroacetylchloride or chloroacetic acid and phosphoryl chloride (Aldrich, Germany) [10, 12, 19, 21]. The commercial trichloroaniline was purified by zone refining. The liquids, trimethylaniline, 2-chloro and 2,2-dichloro acetic acids were purified by double distillation. **TMPMCA** was prepared from 2,4,6-trimethylaniline and 2-chloroacetyl chloride in benzene (chemical analysis: % (found/calculated); C (62.25/62.41), H (6.52/6.67) and N (6.50/6.62)), while **TCPMCA** was prepared from 2,4,6-trichloroaniline and 2-chloroacetyl chloride in acetone. The compounds, **TCPDCA** and **TCPTCA** were prepared by treating 2,4,6-trichloroaniline with a clear mixture of 2,2-dichloroacetic acid / 2,2,2-trichloroacetic acid with phosphoryl chloride under constant stirring. The mixture was slowly warmed to expel HCl. Excess phosphoryl chloride was hydrolysed by adding cold

Table 2 (continued). 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (TCPTCA).

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
Cl(1A)	3058(35)	6660(57)	986(74)	143(9)	Cl(1B)	3167(32)	6311(46)	1144(66)	143(9)
Cl(1C)	3299(47)	5899(47)	1554(42)	143(9)	Cl(1D)	3872(34)	5440(26)	1658(30)	143(9)
Cl(1E)	5730(53)	5767(71)	758(98)	143(9)	Cl(1F)	4933(30)	5398(23)	1276(32)	143(9)
Cl(2A)	6208(32)	6093(38)	682(21)	79(2)	Cl(2B)	6122(32)	6151(38)	500(23)	79(2)
Cl(2C)	3012(16)	7016(19)	848(13)	79(2)	Cl(2D)	5862(50)	5758(38)	975(31)	79(2)
Cl(2E)	3510(24)	7805(27)	479(18)	79(2)	Cl(3A)	5074(43)	8467(31)	28(42)	115(3)
Cl(3B)	4350(21)	8266(16)	231(14)	115(3)	Cl(3C)	5299(43)	8355(35)	–58(42)	115(3)
Cl(3D)	6185(29)	6685(36)	162(24)	115(3)	Cl(3E)	5900(32)	7757(38)	–88(22)	115(3)
C(4)	4685(8)	6920(8)	1129(9)	85(3)	C(5)	4754(9)	7058(9)	2307(8)	62(2)
O(6)	5841(6)	6861(8)	2613(6)	78(2)	N(7)	3565(7)	7418(6)	2926(6)	57(2)
C(8)	3506(7)	7509(7)	4063(7)	51(2)	C(9)	3368(8)	6517(8)	5037(8)	55(2)
C(10)	3390(10)	6528(9)	6144(9)	67(2)	C(11)	3525(10)	7595(10)	6288(9)	69(2)
C(12)	3568(10)	8633(10)	5364(10)	73(3)	C(13)	3601(9)	8578(8)	4240(9)	65(2)
Cl(14)	3227(3)	5157(2)	4854(2)	75(1)	Cl(15)	3524(4)	7655(4)	7679(3)	114(1)
Cl(16)	3744(4)	9860(3)	3086(3)	105(1)	Cl(17)	398(4)	994(3)	5474(3)	92(1)
Cl(18)	2898(2)	2214(2)	5098(2)	71(1)	Cl(19)	308(3)	3535(2)	4779(3)	83(1)
C(20)	1035(9)	2234(7)	5627(7)	54(2)	C(21)	527(8)	2191(7)	6931(7)	51(2)
O(22)	–664(7)	1956(8)	7422(6)	79(2)	N(23)	1494(7)	2408(6)	7419(6)	54(2)
C(24)	1129(8)	2329(8)	8655(7)	54(2)	C(25)	1417(11)	1277(9)	9464(9)	69(2)
C(26)	1134(11)	1168(10)	10671(9)	76(3)	C(27)	563(10)	2119(9)	11014(8)	68(2)
C(28)	242(10)	3161(8)	10237(8)	64(2)	C(29)	539(9)	3256(7)	9047(7)	54(2)
Cl(31)	257(4)	2028(3)	12498(2)	104(1)	Cl(30)	2149(5)	77(3)	8994(4)	116(1)
Cl(32)	199(3)	4589(2)	8043(2)	79(1)					

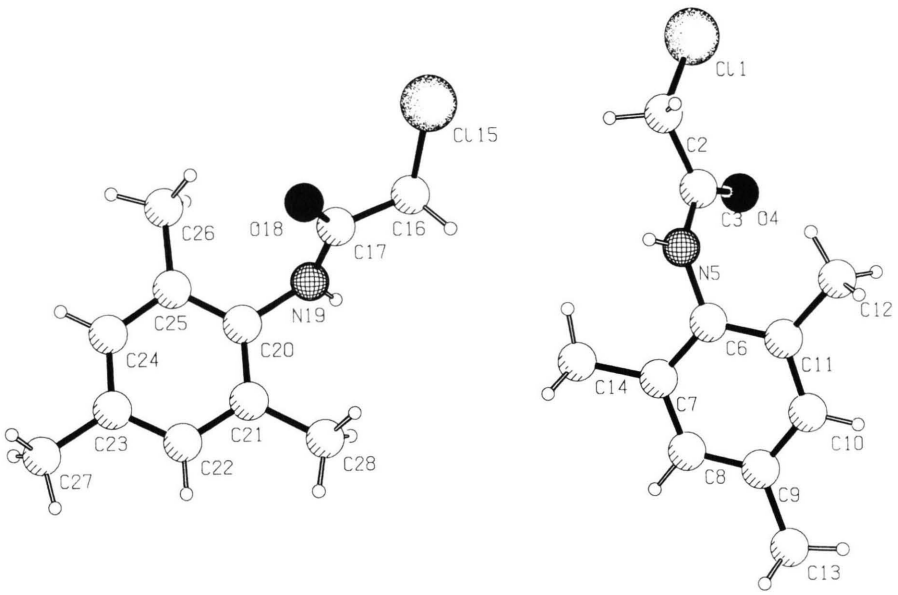

Fig. 1. Molecular geometry of N-(2,4,6-trimethylphenyl)-2-chloroacetamide, 2,4,6-$(CH_3)_3C_6H_2$-NHCO-CH_2Cl (**TMPMCA**), with the numbering of atoms.

water drop wise under ice cold conditions. The solid was filtered under suction, washed thoroughly with water and dried. The compounds were recrystallised from ethanol several times. The purity of the compounds **TCPMCA**, **TCPDCA**, and **TCPTCA** was checked by determining their melting points. The melting points in °C are (the values in parentheses are literature values [19, 21]: (**TCPMCA**) 180 (180);

Table 3. Bond lengths (Å) (standard deviation).

Connection	Bond length	Connection	Bond length
TMPMCA			
Cl(1)-C(2)	1.709(5)	C(2)-C(3)	1.513(6)
C(3)-O(4)	1.228(4)	C(3)-N(5)	1.324(5)
N(5)-C(6)	1.423(5)	C(6)-C(11)	1.394(6)
C(6)-C(7)	1.397(6)	C(7)-C(8)	1.395(6)
C(7)-C(14)	1.495(6)	C(8)-C(9)	1.372(6)
C(9)-C(10)	1.379(7)	C(9)-C(13)	1.502(7)
C(10)-C(11)	1.387(6)	C(11)-C(12)	1.501(7)
Cl(15)-C(16)	1.734(5)	C(16)-C(17)	1.507(6)
C(17)-O(18)	1.233(4)	C(17)-N(19)	1.315(5)
N(19)-C(20)	1.431(5)	C(20)-C(21)	1.386(6)
C(20)-C(25)	1.394(6)	C(21)-C(22)	1.399(7)
C(21)-C(28)	1.502(6)	C(22)-C(23)	1.374(7)
C(23)-C(24)	1.359(7)	C(23)-C(27)	1.497(8)
C(24)-C(25)	1.401(7)	C(25)-C(26)	1.500(7)
TCPMCA			
Cl(1)-C(2)	1.750(5)	C(2)-C(3)	1.514(8)
C(3)-O(4)	1.218(6)	C(3)-N(5)	1.342(7)
N(5)-C(6)	1.408(7)	C(6)-C(7)	1.386(8)
C(6)-C(11)	1.395(7)	C(7)-C(8)	1.372(8)
C(7)-Cl(12)	1.740(5)	C(8)-C(9)	1.389(8)
C(9)-C(10)	1.368(8)	C(9)-Cl(13)	1.744(6)
C(10)-C(11)	1.377(8)	C(11)-Cl(14)	1.733(6)
Cl(15)-C(16)	1.740(6)	C(16)-C(17)	1.511(8)
C(17)-O(18)	1.214(6)	C(17)-N(19)	1.347(7)
N(19)-C(20)	1.407(7)	C(20)-C(21)	1.387(7)
C(20)-C(25)	1.399(7)	C(21)-C(22)	1.368(8)
C(21)-Cl(26)	1.738(5)	C(22)-C(23)	1.361(8)
C(23)-C(24)	1.398(9)	C(23)-Cl(27)	1.726(6)
C(24)-C(25)	1.375(8)	C(25)-Cl(28)	1.728(6)
TCPA			
C(1)-C(2)	1.499(3)	C(2)-O(3)	1.221(3)
C(2)-N(4)	1.351(3)	N(4)-C(5)	1.413(3)
C(5)-C(10)	1.387(3)	C(5)-C(6)	1.398(3)
C(6)-C(7)	1.379(3)	C(6)-Cl(11)	1.722(2)
C(7)-C(8)	1.374(3)	C(8)-C(9)	1.384(3)
C(8)-Cl(12)	1.735(2)	C(9)-C(10)	1.382(3)
C(10)-Cl(13)	1.727(2)		
TCPDCA			
C(3)-Cl(1)	1.754(6)	C(3)-Cl(2)	1.744(6)
C(3)-C(4)	1.511(7)	C(4)-O(5)	1.235(7)
C(4)-N(6)	1.316(7)	O(5)-H(6N)	3.000(6)
C(7)-N(6)	1.417(7)	C(7)-C(8)	1.377(8)
C(7)-C(12)	1.390(8)	C(8)-C(9)	1.385(8)
C(8)-Cl(13)	1.731(6)	C(9)-C(10)	1.384(9)
C(10)-C(11)	1.355(8)	C(10)-Cl(14)	1.732(6)
C(11)-C(12)	1.378(8)	C(12)-Cl(15)	1.734(5)

(**TCPDCA**) 186 (186 - 187); (**TCPTCA**) 119 (118 - 120). The compounds were further characterised by recording their infrared and/or ^{35}Cl NQR spectra and comparing the frequencies with the literature values. All other reagents employed in the preperations and purification of compounds were of analytical grade.

Table 3 (continued).

Connection	Bond length	Connection	Bond length
TCPTCA			
Cl(1A)-C(4)	1.73(2)	Cl(1B)-C(4)	1.73(2)
Cl(1C)-C(4)	1.80(2)	Cl(1D)-C(4)	1.87(2)
Cl(1E)-C(4)	1.73(2)	Cl(1F)-C(4)	1.76(2)
Cl(2A)-C(4)	1.76(2)	Cl(2B)-C(4)	1.74(2)
Cl(2C)-C(4)	1.75(2)	Cl(2D)-C(4)	1.73(2)
Cl(2E)-C(4)	1.65(2)	Cl(3A)-C(4)	1.92(2)
Cl(3B)-C(4)	1.68(2)	Cl(3C)-C(4)	1.90(2)
Cl(3D)-C(4)	1.70(2)	Cl(3E)-C(4)	1.75(2)
C(4)-C(5)	1.526(13)	C(5)-O(6)	1.194(10)
C(5)-N(7)	1.331(11)	O(6)-H(7N)	2.982(9)
N(7)-C(8)	1.422(11)	C(8)-C(9)	1.374(12)
C(8)-C(13)	1.381(12)	C(9)-C(10)	1.369(13)
C(9)-Cl(14)	1.738(8)	C(10)-C(11)	1.368(14)
C(11)-C(12)	1.380(20)	C(11)-Cl(15)	1.733(10)
C(12)-C(13)	1.394(14)	C(13)-Cl(16)	1.707(10)
Cl(17)-C(20)	1.755(8)	Cl(18)-C(20)	1.781(9)
Cl(19)-C(20)	1.755(9)	C(20)-C(21)	1.536(11)
C(21)-O(22)	1.192(10)	C(21)-N(23)	1.333(9)
O(22)-H(23N)	2.998(9)	N(23)-C(24)	1.441(10)
C(24)-C(29)	1.360(12)	C(24)-C(25)	1.377(13)
C(25)-C(26)	1.401(14)	C(25)-Cl(30)	1.731(10)
C(26)-C(27)	1.350(20)	C(27)-C(28)	1.360(14)
C(27)-Cl(31)	1.739(9)	C(28)-C(29)	1.384(12)
C(29)-Cl(32)	1.727(8)		

Table 4. Bond angles (degree) (standard deviation).

Connection	Bond angle	Connection	Bond angle
TMPMCA			
C(3)-C(2)-Cl(1)	113.8(3)	O(4)-C(3)-N(5)	123.8(4)
O(4)-C(3)-C(2)	121.3(4)	N(5)-C(3)-C(2)	114.9(3)
C(3)-N(5)-C(6)	123.2(3)	C(7)-C(6)-N(5)	118.6(4)
C(11)-C(6)-N(5)	119.7(4)	C(11)-C(6)-C(7)	121.7(4)
C(8)-C(7)-C(6)	117.3(4)	C(8)-C(7)-C(14)	121.0(4)
C(6)-C(7)-C(14)	121.7(4)	C(9)-C(8)-C(7)	122.8(4)
C(8)-C(9)-C(10)	117.6(4)	C(8)-C(9)-C(13)	121.4(5)
C(10)-C(9)-C(13)	121.0(5)	C(9)-C(10)-C(11)	122.9(4)
C(10)-C(11)-C(6)	117.5(4)	C(10)-C(11)-C(12)	120.9(4)
C(6)-C(11)-C(12)	121.5(4)		
C(17)-C(16)-Cl(15)	113.9(3)	O(18)-C(17)-N(19)	124.2(4)
O(18)-C(17)-C(16)	121.3(4)	N(19)-C(17)-C(16)	114.5(3)
C(17)-N(19)-C(20)	124.6(3)	C(21)-C(20)-C(25)	121.3(4)
C(21)-C(20)-N(19)	119.1(4)	C(25)-C(20)-N(19)	119.6(4)
C(20)-C(21)-C(22)	118.3(4)	C(20)-C(21)-C(28)	121.1(4)
C(22)-C(21)-C(28)	120.5(4)	C(23)-C(22)-C(21)	121.9(5)
C(24)-C(23)-C(22)	118.1(5)	C(24)-C(23)-C(27)	120.5(5)
C(22)-C(23)-C(27)	121.3(5)	C(23)-C(24)-C(25)	123.2(4)
C(20)-C(25)-C(24)	117.2(4)	C(20)-C(25)-C(26)	121.9(4)
C(24)-C(25)-C(26)	120.8(4)		

Crystal Structure Studies

Small crystals of **TMPMCA**, **TCPMCA**, **TCPDCA** and **TCPTCA** were selected for X-ray

Table 4 (continued).

Connection	Bond angle	Connection	Bond angle
TCPMCA			
C(3)-C(2)-Cl(1)	111.8(3)	O(4)-C(3)-N(5)	123.1(5)
O(4)-C(3)-C(2)	122.8(5)	N(5)-C(3)-C(2)	114.1(4)
C(3)-N(5)-C(6)	122.8(4)	C(7)-C(6)-N(5)	121.5(5)
C(11)-C(6)-N(5)	122.2(5)	C(7)-C(6)-C(11)	116.4(5)
C(8)-C(7)-C(6)	123.4(5)	C(8)-C(7)-Cl(12)	117.9(4)
C(6)-C(7)-Cl(12)	118.7(4)	C(7)-C(8)-C(9)	117.3(5)
C(10)-C(9)-C(8)	122.3(5)	C(10)-C(9)-Cl(13)	119.2(5)
C(8)-C(9)-Cl(13)	118.5(4)	C(9)-C(10)-C(11)	118.2(5)
C(10)-C(11)-C(6)	122.4(5)	C(10)-C(11)-Cl(14)	117.5(4)
C(6)-C(11)-Cl(14)	120.1(4)		
C(17)-C(16)-Cl(15)	112.8(4)	O(18)-C(17)-N(19)	123.9(5)
O(18)-C(17)-C(16)	122.5(5)	N(19)-C(17)-C(16)	113.6(4)
C(17)-N(19)-C(20)	123.1(4)	C(21)-C(20)-C(25)	116.5(5)
C(21)-C(20)-N(19)	121.8(5)	C(25)-C(20)-N(19)	121.6(5)
C(22)-C(21)-C(20)	122.9(5)	C(22)-C(21)-Cl(26)	118.7(4)
C(20)-C(21)-Cl(26)	118.4(4)	C(23)-C(22)-C(21)	119.1(5)
C(22)-C(23)-C(24)	120.9(5)	C(22)-C(23)-Cl(27)	120.7(5)
C(24)-C(23)-Cl(27)	118.4(4)	C(25)-C(24)-C(23)	118.6(5)
C(24)-C(25)-C(20)	121.8(5)	C(24)-C(25)-Cl(28)	117.4(4)
C(20)-C(25)-Cl(28)	120.8(4)		
TCPDCA			
C(4)-C(3)-Cl(2)	108.5(4)	C(4)-C(3)-Cl(1)	111.1(4)
Cl(2)-C(3)-Cl(1)	110.4(3)	O(5)-C(4)-N(6)	124.4(5)
O(5)-C(4)-C(3)	120.1(5)	N(6)-C(4)-C(3)	115.4(5)
C(8)-C(7)-C(12)	117.4(5)	C(8)-C(7)-N(6)	121.1(5)
C(12)-C(7)-N(6)	121.4(5)	C(7)-C(8)-C(9)	122.3(5)
C(7)-C(8)-Cl(13)	119.2(4)	C(9)-C(8)-Cl(13)	118.5(5)
C(10)-C(9)-C(8)	117.9(5)	C(11)-C(10)-C(9)	121.3(5)
C(11)-C(10)-Cl(14)	120.1(5)	C(9)-C(10)-Cl(14)	118.6(4)
C(10)-C(11)-C(12)	119.8(5)	C(11)-C(12)-C(7)	121.2(5)
C(11)-C(12)-Cl(15)	118.6(4)	C(7)-C(12)-Cl(15)	120.3(4)
C(4)-N(6)-C(7)	124.4(4)		
TCPA			
O(3)-C(2)-N(4)	123.2(2)	O(3)-C(2)-C(1)	122.0(2)
N(4)-C(2)-C(1)	114.8(2)	C(2)-N(4)-C(5)	123.2(2)
C(10)-C(5)-C(6)	117.3(2)	C(10)-C(5)-N(4)	122.5(2)
C(6)-C(5)-N(4)	120.1(2)	C(7)-C(6)-C(5)	121.9(2)
C(7)-C(6)-Cl(11)	119.1(2)	C(5)-C(6)-Cl(11)	119.0(2)
C(8)-C(7)-C(6)	118.5(2)	C(7)-C(8)-C(9)	121.9(2)
C(7)-C(8)-Cl(12)	119.1(2)	C(9)-C(8)-Cl(12)	119.0(2)
C(10)-C(9)-C(8)	118.2(2)	C(9)-C(10)-C(5)	122.1(2)
C(9)-C(10)-Cl(13)	118.1(2)	C(5)-C(10)-Cl(13)	119.8(2)

Table 4 (continued). TCPTCA.

Connection	Bond angle	Connection	Bond angle
C(5)-C(4)-Cl(1A)	117.0(3)	C(5)-C(4)-Cl(1B)	115.0(2)
C(5)-C(4)-Cl(1E)	115.0(3)	C(5)-C(4)-Cl(2A)	107.0(9)
C(5)-C(4)-Cl(2B)	114.9(11)	C(5)-C(4)-Cl(2C)	116.7(8)
C(5)-C(4)-Cl(2D)	104.3(12)	C(5)-C(4)-Cl(2E)	114.8(9)
C(5)-C(4)-Cl(3B)	107.9(9)	C(5)-C(4)-Cl(3D)	120.4(14)
C(5)-C(4)-Cl(3E)	113.8(13)	Cl(1A)-C(4)-Cl(2A)	122.0(2)
Cl(1B)-C(4)-Cl(2B)	108.0(2)	Cl(2E)-C(4)-Cl(1E)	130.0(3)
Cl(3D)-C(4)-Cl(2C)	123.0(2)	O(6)-C(5)-N(7)	124.0(8)
O(6)-C(5)-C(4)	119.8(8)	N(7)-C(5)-C(4)	116.2(7)
C(5)-N(7)-C(8)	120.3(7)	C(9)-C(8)-C(13)	117.2(8)
C(9)-C(8)-N(7)	120.6(7)	C(13)-C(8)-N(7)	122.2(8)
C(10)-C(9)-C(8)	123.7(8)	C(10)-C(9)-Cl(14)	117.6(7)
C(8)-C(9)-Cl(14)	118.6(7)	C(11)-C(10)-C(9)	117.8(9)
C(10)-C(11)-C(12)	121.2(9)	C(10)-C(11)-Cl(15)	119.4(8)
C(12)-C(11)-Cl(15)	119.3(8)	C(11)-C(12)-C(13)	119.0(8)
C(8)-C(13)-C(12)	120.7(9)	C(8)-C(13)-Cl(16)	120.4(8)
C(12)-C(13)-Cl(16)	118.8(7)	C(21)-C(20)-Cl(17)	107.8(6)
C(21)-C(20)-Cl(18)	114.5(5)	C(21)-C(20)-Cl(19)	107.5(6)
Cl(17)-C(20)-Cl(18)	108.2(5)	Cl(17)-C(20)-Cl(19)	109.8(4)
Cl(19)-C(20)-Cl(18)	109.0(5)	O(22)-C(21)-N(23)	125.7(8)
O(22)-C(21)-C(20)	118.7(7)	N(23)-C(21)-C(20)	115.7(7)
C(21)-N(23)-C(24)	119.4(7)	C(29)-C(24)-C(25)	119.0(8)
C(29)-C(24)-N(23)	122.6(7)	C(25)-C(24)-N(23)	118.4(8)
C(24)-C(25)-C(26)	120.6(9)	C(24)-C(25)-Cl(30)	120.1(8)
C(26)-C(25)-Cl(30)	119.3(8)	C(27)-C(26)-C(25)	118.1(9)
C(26)-C(27)-C(28)	122.5(9)	C(26)-C(27)-Cl(31)	119.2(8)
C(28)-C(27)-Cl(31)	118.3(8)	C(27)-C(28)-C(29)	118.6(9)
C(24)-C(29)-C(28)	121.1(8)	C(24)-C(29)-Cl(32)	119.6(6)
C(28)-C(29)-Cl(32)	119.2(7)		

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) [22 - 27]. For locating the hydrogen atom positions, the C-H distances were fixed to 0.93 Å for the ring hydrogen atoms, while the side chain C-H distances were fixed to 0.96 Å for the CH_3 group, to 0.97 Å for the CH_2Cl group and to 0.98 Å for the $CHCl_2$ group. Further experimental conditions for structure determinations and refinements are given in Table 1. For comparison purposes, the compound N-(2,4,6-trichlorophenyl)-acetamide (**TCPA**) was also prepared and the crystal structures of this compound and 2,4,6-trichloroaniline (**TCA**) have been determined under identical condition.

Results and Discussion

The crystallographic data for **TMPMCA**, **TCPMCA**, **TCPDCA**, and **TCPTCA** are given in Table 1. The atomic coordinates and the mean displacement parameters are listed in Table 2. The intramolecular bond distances and bond angles are given in Tables 3 and 4, respectively. Table 5 lists the dihedral angles of **TCPDCA** and **TCPTCA**. The hydrogen coordinates, anisotropic displacement parameters and further information on the crystal structure determinations have been deposited at the Cambridge Crystallographic Data Centre, the CCDC numbers are 147743 - 147746. In Figs. 1, 3, 5 and 7 we

Table 5. Dihedral angles (degree) (standard deviations).

Connection	Angle	Connection	Angle	Connection	Angle
2,4,6-$Cl_3C_6H_2$.NHCO.$CHCl_2$ (TCPDCA)					
Cl(2)-C(3)-C(4)-O(5)	–90.2(6)	Cl(1)-C(3)-C(4)-O(5)	31.3(7)	Cl(2)-C(3)-C(4)-N(6)	87.5(5)
Cl(1)-C(3)-C(4)-N(6)	–151.1(4)	C(12)-C(7)-C(8)-C(9)	–0.6(8)	N(6)-C(7)-C(8)-C(9)	178.6(5)
C(12)-C(7)-C(8)-Cl(13)	179.2(4)	N(6)-C(7)-C(8)-Cl(13)	–1.6(7)	C(7)-C(8)-C(9)-C(10)	–1.5(8)
Cl(13)-C(8)-C(9)-C(10)	178.7(4)	C(8)-C(9)-C(10)-C(11)	2.6(8)	C(8)-C(9)-C(10)-Cl(14)	–177.2(4)
C(9)-C(10)-C(11)-C(12)	–1.6(9)	Cl(14)-C(10)-C(11)-C(12)	178.2(5)	C(10)-C(11)-C(12)-C(7)	–0.6(8)
C(10)-C(11)-C(12)-Cl(15)	177.7(5)	C(8)-C(7)-C(12)-C(11)	1.7(7)	N(6)-C(7)-C(12)-C(11)	–177.5(5)
C(8)-C(7)-C(12)-Cl(15)	–176.6(4)	N(6)-C(7)-C(12)-Cl(15)	4.2(7)	O(5)-C(4)-N(6)-C(7)	2.1(9)
C(3)-C(4)-N(6)-C(7)	–175.4(5)	C(8)-C(7)-N(6)-C(4)	–117.9(6)	C(12)-C(7)-N(6)-C(4)	61.2(7)
2,4,6-$Cl_3C_6H_2$.NHCO.CCl_3 (TCPTCA)					
Cl(2E)-C(4)-C(5)-O(6)	–150.0(2)	Cl(3B)-C(4)-C(5)-O(6)	–114.2(12)	Cl(3D)-C(4)-C(5)-O(6)	–9(2)
Cl(3E)-C(4)-C(5)-O(6)	–56(2)	Cl(1A)-C(4)-C(5)-O(6)	156(3)	Cl(1B)-C(4)-C(5)-O(6)	141(2)
Cl(2A)-C(4)-C(5)-O(6)	16(2)	Cl(2B)-C(4)-C(5)-O(6)	14(2)	Cl(1E)-C(4)-C(5)-O(6)	36(4)
Cl(2C)-C(4)-C(5)-O(6)	171(11)	Cl(2D)-C(4)-C(5)-O(6)	34(2)	Cl(1E)-C(4)-C(5)-N(7)	–145(4)
Cl(2E)-C(4)-C(5)-N(7)	29(2)	Cl(3E)-C(4)-C(5)-N(7)	123(2)	Cl(3B)-C(4)-C(5)-N(7)	64.8(11)
Cl(3D)-C(4)-C(5)-N(7)	170(2)	Cl(1A)-C(4)-C(5)-N(7)	–25(3)	Cl(1B)-C(4)-C(5)-N(7)	–40(2)
Cl(2C)-C(4)-C(5)-N(7)	–10.0(14)	Cl(2D)-C(4)-C(5)-N(7)	–147(2)	Cl(2A)-C(4)-C(5)-N(7)	–165(2)
Cl(2B)-C(4)-C(5)-N(7)	–167(2)	O(6)-C(5)-N(7)-C(8)	–4.6(14)	C(4)-C(5)-N(7)-C(8)	176.5(7)
C(5)-N(7)-C(8)-C(9)	–78.8(10)	C(5)-N(7)-C(8)-C(13)	100.3(10)	C(13)-C(8)-C(9)-C(10)	–3.3(12)
N(7)-C(8)-C(9)-C(10)	175.9(8)	C(13)-C(8)-C(9)-Cl(14)	179.4(6)	N(7)-C(8)-C(9)-Cl(14)	–1.5(10)
C(8)-C(9)-C(10)-C(11)	1.5(13)	Cl(14)-C(9)-C(10)-C(11)	179.0(7)	C(9)-C(10)-C(11)-C(12)	3.1(14)
C(9)-C(10)-C(11)-Cl(15)	178.8(7)	C(10)-C(11)-C(12)-C(13)	–5.8(14)	Cl(15)-C(11)-C(12)-C(13)	178.5(7)
C(9)-C(8)-C(13)-C(12)	0.4(12)	N(7)-C(8)-C(13)-C(12)	–178.7(8)	C(9)-C(8)-C(13)-Cl(16)	–178.9(6)
N(7)-C(8)-C(13)-Cl(16)	2.0(11)	C(11)-C(12)-C(13)-C(8)	4.0(14)	C(11)-C(12)-C(13)-Cl(16)	–176.7(8)
Cl(17)-C(20)-C(21)-O(22)	–44.3(10)	Cl(19)-C(20)-C(21)-O(22)	74.0(9)	Cl(18)-C(20)-C(21)-O(22)	–164.7(7)
Cl(17)-C(20)-C(21)-N(23)	134.6(7)	Cl(19)-C(20)-C(21)-N(23)	–107.1(7)	Cl(18)-C(20)-C(21)-N(23)	14.2(10)
O(22)-C(21)-N(23)-C(24)	1.9(13)	C(20)-C(21)-N(23)-C(24)	–176.9(7)	C(21)-N(23)-C(24)-C(29)	–87.1(10)
C(21)-N(23)-C(24)-C(25)	94.1(10)	C(29)-C(24)-C(25)-C(26)	–1.2(14)	N(23)-C(24)-C(25)-C(26)	177.5(8)
C(29)-C(24)-C(25)-Cl(30)	179.2(7)	N(23)-C(24)-C(25)-Cl(30)	–2.0(11)	C(24)-C(25)-C(26)-C(27)	1(2)
Cl(30)-C(25)-C(26)-C(27)	180.0(8)	C(25)-C(26)-C(27)-C(28)	1(2)	C(25)-C(26)-C(27)-Cl(31)	–177.7(8)
C(26)-C(27)-C(28)-C(29)	–1(2)	Cl(31)-C(27)-C(28)-C(29)	177.3(7)	C(25)-C(24)-C(29)-C(28)	0.8(13)
N(23)-C(24)-C(29)-C(28)	–177.9(7)	C(25)-C(24)-C(29)-Cl(32)	178.8(7)	N(23)-C(24)-C(29)-Cl(32)	0.1(11)
C(27)-C(28)-C(29)-C(24)	0.5(13)	C(27)-C(28)-C(29)-Cl(32)	–177.6(7)		

show the molecules of the title compounds as they appear in suitable projection with the numbering of the atoms used throughout the paper. The projections of the unit cells of **TMPMCA**, **TCPMCA**, **TCPDCA**, and **TCPTCA** are shown in Figures 2, 4, 6 and 8, respectively.

TMPMCA, **TCPMCA**, and **TCPTCA** show two molecules each in their asymmetric units. This is in agreement with the multiple lines observed in the ^{35}Cl NQR spectrum of **TCPTCA** [19]. Further, this compound shows disorder as indicated by the multiplicity of the C(side chain) - Cl bonds. **TCPTCA** does not show ^{35}Cl NQR spectra, while **TMPMCA** shows single frequency which fades out above 200 K, indicating that it may undergo phase transition well below room temperature. First we shall discuss the intramolecular geometry of the four title compounds. The individual data are given in Tables 3 and 4. Comparing the C(i)-C(j) bond distances within the benzene rings of the four compounds we find the following mean distances in angstrom units. The observed minimum and maximum bond lengths in Å are given in parentheses.: 1.386 (1.359, 1.401), 1.381 (1.361, 1.399), 1.378 (1.355, 1.390) and 1.375 (1.350, 1.401) Å for the compounds **TMPMCA**, **TCPMCA**, **TCPDCA**, and **TCPTCA**, respectively. We have also determined the crystal structures of **TCA** and **TCPA** under the present experimental conditions and find the mean ring distance in them as 1.386 (1.367, 1.399) Å and 1.384 (1.374, 1.398) Å, respectively. As may be seen, conversion of **TCA** into **TCPA** and gradual replacement of H-atoms in the side chain of the latter to give the compounds **TCPMCA**, **TCPDCA**, and **TCPTCA** with the side chains $-CH_2Cl$, $-CHCl_2$ and $-CCl_3$, respectively, slightly decreases the mean ring distances of these compounds. Changes in the

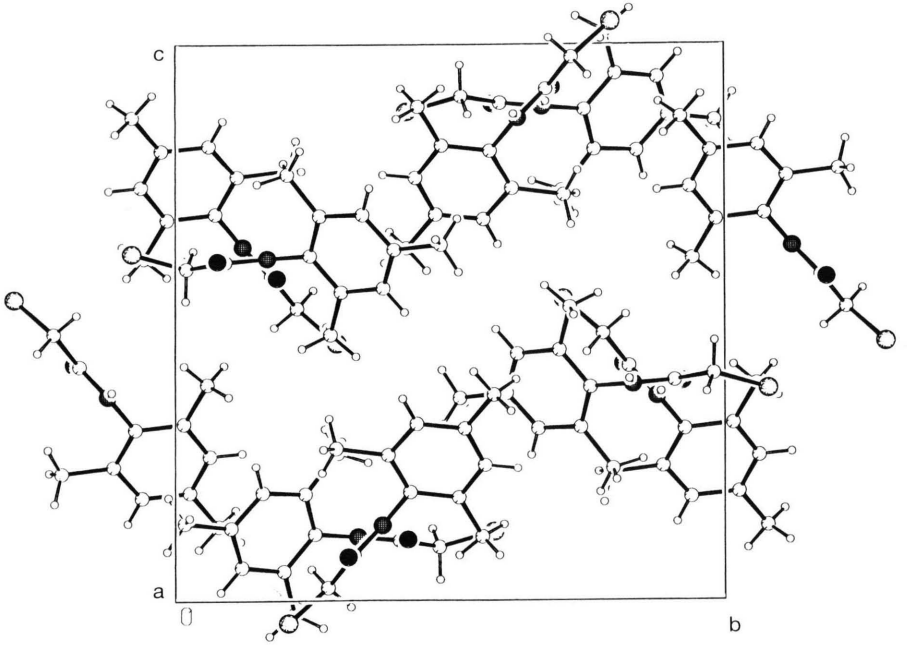

Fig. 2. Projection of the unit cell of **TMPMCA** along [100] on to the *bc* plane.

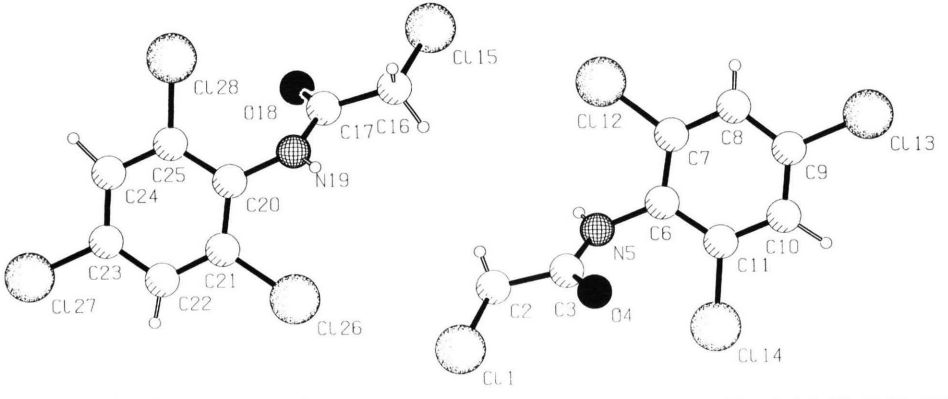

Fig. 3. Molecular geometry of N-(2,4,6-trichlorophenyl)-2-chloroacetamide, 2,4,6-$Cl_3C_6H_2$-NHCO-CH_2Cl (**TCPMCA**), with the numbering of atoms.

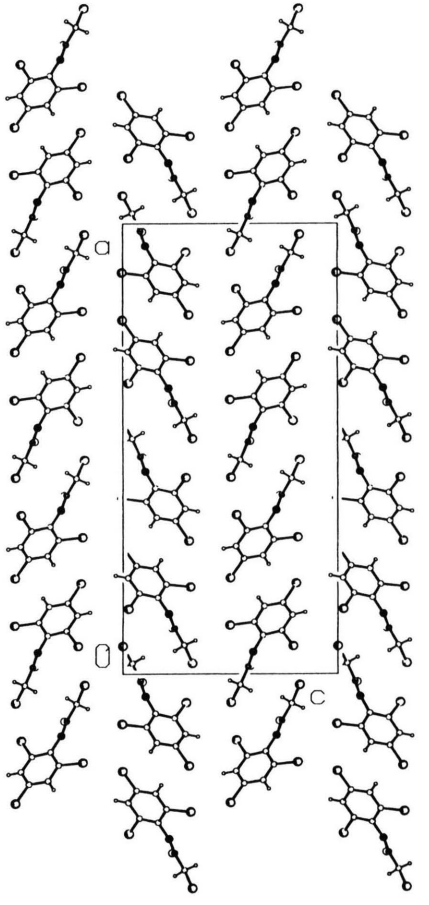

Fig. 4. Projection of the unit cell of **TCPMCA** along [101] on to the *ac* plane.

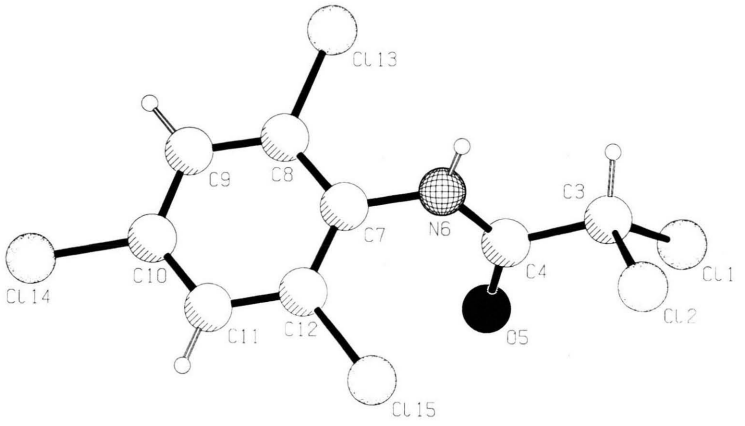

Fig. 5. Molecular geometry of N-(2,4,6-trichlorophenyl)-2,2-dichloroacetamide, $2,4,6\text{-}Cl_3C_6H_2\text{-}NHCO\text{-}CHCl_2$ (**TCPDCA**), with the numbering of atoms.

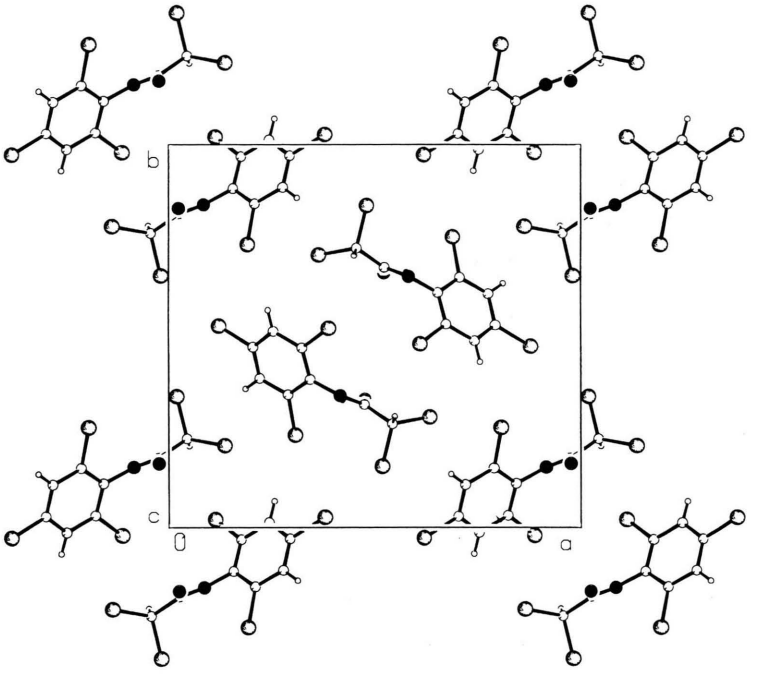

Fig. 6. Projection of the unit cell of **TCPDCA** along [110] on to the *ab* plane.

mean ring distances are smaller as the effect has to be transmitted through the peptide linkage. Further, the mean ring distances of **TMPMCA** and **TCPMCA** are 1.386 and 1.381 Å, respectively, indicating that the replacement of 3 Cl (electron withdrawing) atoms by 3 CH_3 (electron donating) groups in the ring increases the mean ring distance. The C(ring)-Cl and the C(ring) - N distances for **TCA**, **TCPA**, **TMPMCA**, **TCPMCA**, **TCPDCA**, and **TCPTCA** do not show regular trends.

As regards the bond angles, they are observed between 115.1° and 123.3° (**TCA**), 117.3° and 122.1° (**TCPA**), 117.2 and 123.2° (**TMPMCA**), 116.5° and 123.2° (**TCPMCA**), 117.4° and 122.3° (**TCPDCA**) 118.0° and 122.2° (**TCPTCA**). The C2(ring)-C1(ring)-N and C6(ring)-C1(ring)-N angles for the compounds are 122.4° and 122.0° (**TCA**), 120.1° and 122.5° (**TCPA**), 118.9 and 119.7° (**TMPMCA**), 121.7° and 121.9° (**TCPMCA**), 121.1° and 121.4° (**TCPDCA**), 119.5° and 122.4° (**TCPTCA**). Similarly the C2(ring)-C1(ring)-C6(ring) bond angles are 115.6°, 117.3°, 121.5°, 116.5°, 117.4° and 118.1° for **TCA**, **TCPA**, **TMPMCA**, **TCPMCA**, **TCPDCA** and **TCPTCA**, respectively, while the C(ring)-N-C(O) bond angles vary as 123.2° (**TCPA**), 123.9° (**TMPMCA**),

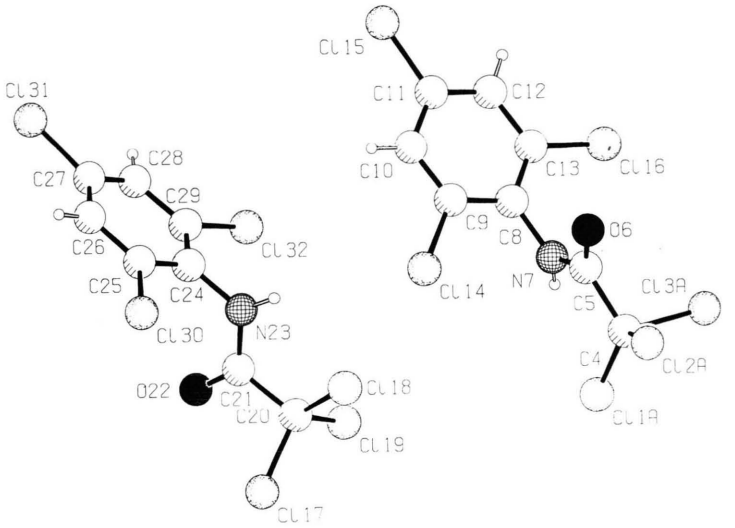

Fig. 7. Molecular geometry of N-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide, 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (**TCPTCA**), with the numbering of atoms.

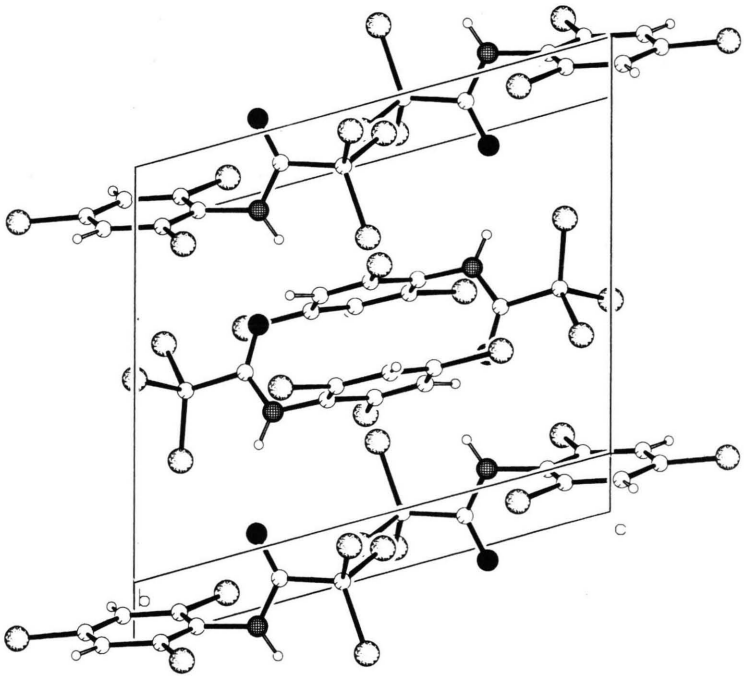

Fig. 8. Projection of the unit cell of **TCPTCA** along [101] on to the *ac* plane.

123.0° (**TCPMCA**), 124.4° (**TCPDCA**) and 119.9° (**TCPTCA**). The N-C(O)-C(side chain) angles are 114.8° (**TCPA**),114.7° (**TMPMCA**), 113.9° (**TCPMCA**), 115.4° (**TCPDCA**) and 116.0° (**TCPTCA**), respectively.

We have recently determined the crystal structures of several N-phenyl and N-(mono-substituted phenyl)-2,2-dichloroacetamides and 2,2,2-trichloroacetamides [18]. Hence we compare here the present crystal structure data on **TMPMCA**, **TCPMCA**, **TCPDCA** and **TCPTCA** with the above data. We shall first compare the results of 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (**TCPTCA**) with 2,6-$Cl_2C_6H_3$-NHCO-CCl_3 (**DCPTCA**) [28], 2-ClC_6H_4-NHCO-CCl_3 (**MCPTCA**) [18] and C_6H_5-NHCO-CCl_3 (**PTCA**) [11]. The average ring C-C bond distances in Å are (minimum and maximum bond distances are shown in parentheses) 1.372 (1.350, 1.401) (**TCPTCA**); 1.380 (1.372, 1.385) (**DCPTCA**), 1.383 (1.368, 1.391) (**MCPTCA**), 1.383 (1.373, 1.390)

(**PTCA**). There are no significant changes in the other bond distances on going from (**PTCA**) to (**TCPTCA**), except for C(O)-C(side chain) bond distances which decrease slightly as we go from C_6H_5-NHCO-CCl_3 (**PTCA**) to 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (**TCPTCA**): 1.564 Å (**PTCA**), 1.561Å (**MCPTCA**), 1.550 Å (**DCPTCA**) and 1.531Å (**TCPTCA**). The C(ring)-N-C(O) and N-C(O)-C(side chain) bond angles show slight decreasing and increasing trends as we go from C_6H_5-NHCO-CCl_3 (**PTCA**) to 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (**TCPTCA**): 125.4°, 114.8° (**PTCA**), 122.4°, 114.1° (**MCPTCA**), 121.4°. 114.8° (**DCPTCA**) and 119.9°, 116° (**TCPTCA**).

Comparison of the crystal structure data of 2,4,6-$Cl_3C_6H_2$-NHCO-$CHCl_2$ (**TCPDCA**) with 2-ClC_6H_4-NHCO-$CHCl_2$ (**MCPDCA**) and C_6H_5-NHCO-$CHCl_2$ (**PDCA**) revealed similar trends. The average C-C ring distances in Å are 1.384 (**PDCA**), 1.379 (**MCPDCA**) and 1.378 (**TCPDCA**). The other side chain distances generally show a slightly decreasing trend as we go from **PDCA** to **TCPDCA**. The C(ring)-N-C(O), O-C(O)-N and O-C(O)-C (side chain) bond angles show similar trends as we go from C_6H_5-NHCO-$CHCl_2$ to 2,4,6-$Cl_3C_6H_2$-NHCO-$CHCl_2$, while the N-C(O)-C(side chain) bond angle increases by about 2°.

The following observations may be made from the careful analysis of the available crystal structure data [11, 12, 17, 18, 20, 28, 29], but to draw general conclusions extensive data are to be collected. Our work in this direction is in progress: N-phenyl acetamide (**PA**) on conversion to either **PTCA** or **TCPA** by side chain or ring substitution changes it's crystal symmetry from orthorhombic to the monoclinic. But both the side chain and ring substitutions of **PA** converts it into **TCPTCA**, and it's orthorhombic symmetry is changed to the triclinic symmetry. On conversion of **PTCA** to **TCPTCA** through mono and di ring substitutions (**MCPTCA** and **DCPTCA**), the crystal symmetry changes from monoclinic to triclinic via orthorhombic and monoclinic symmetries, while conversion of **TCPA** to **TCPTCA** via mono and di- side chain substitutions by Cl (**TCPMCA** and **TCPDCA**), changes it's crystal symmetry from monoclinic to triclinic through orthorhombic symmetries twice.

The molecules in 2,4,6-$Cl_3C_6H_2$-NHCO-$CHCl_2$ (**TCPDCA**) and 2,4,6-$Cl_3C_6H_2$-NHCO-CCl_3 (**TCPTCA**) are linked in chains by -NH–O- hydrogen bonds (about 3 Å) between the amide groups of the molecules.

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