Effect of *Meta*-Substitution on Solid State Geometry of *N*-(Aryl)-2,2,2-trichloro-acetamides, 3-XC_6H_4NH-CO-CCl_3 and 3,5-$X_2C_6H_3NH$-CO-CCl_3 (X = Cl, CH_3)

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The crystal structures of *N*-(*meta*-substituted phenyl)-2,2,2-trichloro-acetamides such as *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-CCl_3 (**3MPTCA**); *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide, 3-ClC_6H_4NH-CO-CCl_3 (**3CPTCA**); *N*-(3,5-dimethylphenyl)-2,2,2-trichloro-acetamide, 3,5-$(CH_3)_2C_6H_3NH$-CO-CCl_3 (**35DMPTCA**) and *N*-(3,5-dichlorophenyl)-2,2,2-trichloro-acetamide, 3,5-$Cl_2C_6H_3NH$-CO-CCl_3 (**35DCPTCA**) have been determined at room temperature. The crystal system, space group, formula units and lattice constants (Å) of the new structures are: **3MPTCA**: orthorhombic, *Pbca*, $Z = 8$, $a = 12.3199(11)$, $b = 8.9719(8)$, $c = 20.2058(15)$; **3CPTCA**: orthorhombic, *Fdd*2, $Z = 16$, $a = 19.285(4)$, $b = 40.765(8)$, $c = 5.5920(11)$; **35DMPTCA**: triclinic, $P\bar{1}$, $Z = 2$, $a = 8.994(4)$, $b = 9.9890(10)$, $c = 14.760(5)$, $\alpha = 79.56(2)^\circ$, $\beta = 73.32(3)^\circ$, $\gamma = 86.47(2)^\circ$; and **35DCPTCA**: orthorhombic, *Pbca*, $Z = 8$, $a = 22.485(5)$, $b = 10.738(2)$, $c = 10.028(3)$. The compound **35DMPTCA** has two molecules in its asymmetric unit, similar to *o*-NO_2-, *m*-NO_2- and *p*-CH_3-substituted phenyl-trichloro-acetamides, while **3MPTCA**, **3CPTCA** and **35DCPTCA** have one molecule each in their asymmetric units. The analysis of data indicates that the substitution of a strong electron withdrawing group such as a nitro group into **PTCA** at *ortho* or *meta* positions has a significant effect on the crystal parameters.

Key words: Meta-Substitution; Crystal Geometry; *N*-(Aryl)-trichloro-acetamides.

1. Introduction

Nuclear quadrupole resonance and crystal structure studies give valuable informations on bond properties. The combined tool of NQR spectroscopy and XRD has been extensively used to investigate the structure of a variety of compounds including amides [1 – 17]. Amides are of fundamental chemical interest as conjugation between the nitrogen lone pair electrons and the carbonyl π-bond, resulting in distinct physical and chemical properties. The amide moiety is an important constituent of many biologically significant compounds. We are interested in structural studies of amides in their crystalline state, using this combined tool [3 – 17]. We have recently prepared several substituted amides of the configuration $X_yC_6H_{5-y}NH$-CO-$CH_{3-y}Cl_y$ (where X = CH_3, NO_2 or Br and $y = 1$, 2 or 3), and measured their ^{35}Cl NQR spectra [3 – 8, 10, 12]. We have also studied the influence of methyl- and mixed group substitution in the phenyl ring on the $^{35}Cl(\omega)$ NQR. In this process, some interesting features were observed. For example, *N*-(2-methylphenyl)-2,2,2-trichloro-acetamide, *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide and *N*-(4-methylphenyl)-2,2,2-trichloro-acetamide showed, respectively, 1, 3 and 6 $^{35}Cl(\omega)$ NQR frequencies for the same 3 $Cl(\omega)$ atoms present in all the 3 compounds, while the corresponding nitro-substituted compounds, namely *N*-(2-nitrophenyl)-2,2,2-trichloro-acetamide, *N*-(3-nitrophenyl)-2,2,2-trichloro-acetamide and *N*-(4-nitrophenyl)-2,2,2-trichloro-acetamide showed 6, 3, and 3 $^{35}Cl(\omega)$ NQR frequencies for the 3 $Cl(\omega)$ atoms, each present in all the 3 compounds. Some of the corresponding *N*-chloro compounds have also been prepared, and their ^{35}Cl(N) and $^{35}Cl(\omega)$ NQR spectra were measured. Thus we thought it interesting to determine the crystal structures of different amides, to see how the -NHCO- bond parameters vary with sub-

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-CCl_3 (**3MPTCA**); *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide, 3-ClC_6H_4NH-CO-CCl_3 (**3CPTCA**); *N*-(3,5-dimethylphenyl)-2,2,2-trichloro-acetamide, 3,5-$(CH_3)_2C_6H_3NH$-CO-CCl_3 (**35DMPTCA**) and *N*-(3,5-dichlorophenyl)-2,2,2-trichloro-acetamide, 3,5-$Cl_2C_6H_3NH$-CO-CCl_3 (**35DCPTCA**). Diffractometer: Stoe-Stadi 4; monochromator: graphite (002); scan 2 $\theta/\omega = 1/1$; refinement method: full-matrix least-squares on F^2.

Description	**3MPTCA**	**3CPTCA**	**35DMPTCA**	**35DCPTCA**
Chemical formula	$C_9H_8Cl_3NO$	$C_8H_5Cl_4NO$	$C_{20}H_{20}Cl_6N_2O_2$	$C_8H_4Cl_5NO$
Formula mass, g mol^{-1}	252.51	272.93	533.08	307.38
Temperature, K	293(2)	304(2)	301(2)	300(2)
Wavelength, pm	71.073	71.073	71.069	71.073
Crystal system	orthorhombic	orthorhombic	triclinic	orthorhombic
Space group	*Pbca*	*Fdd*2	$P\bar{1}$	*Pbca*
a, Å	12.3199(11)	19.285(4)	8.994(4)	22.485(5)
b, Å	8.9719(8)	40.765(8)	9.9890(10)	10.738(2)
c, Å	20.2058(15)	5.5920(11)	14.760(5)	10.028(3)
α, deg.	90.018(7)	90	79.56(2)	90
β, deg.	90.004(7)	90	73.32(3)	90
γ, deg.	90.002(7)	90	86.47(2)	90
Volume, Å^3	2233.4(3)	4396.2(15)	1249.2(7)	2421.2(10)
Z	8	16	2	8
Density (calculated), g cm^{-3}	1.502	1.649	1.417	1.686
Absorption coefficient, cm^{-1}	7.86	10.41	7.07	10.79
F(000)	1024	2176	544	1216
Crystal size, mm^3	$0.51 \times 0.08 \times 0.07$	$0.55 \times 0.45 \times 0.14$	$0.63 \times 0.17 \times 0.13$	$0.63 \times 0.13 \times 0.08$
θ Range, deg.	4.13 to 25.03	4.08 to 26.36	1.46 to 27.10	1.81 to 25.47
Index ranges	$-14 \le h \le 14$, $-6 \le k \le 10$, $-24 \le l \le 24$	$-10 \le h \le 23$, $-48 \le k \le 25$, $-6 \le l \le 4$	$-11 \le h \le 1$, $-12 \le k \le 11$, $-18 \le l \le 16$	$-27 \le h \le 0$, $-12 \le k \le 0$, $-12 \le l \le 12$
Reflections collections	12776	1878	4577	4340
Independent reflected	1964	1044	4351	2243
R(int)	0.0575	0.0647	0.0145	0.0295
Completeness to 2θ	99.3%	81.3%	78.8%	99.9%
Max. and min. transmission	0.9637 and 1.0000	0.8781 and 1.0000	0.9168 and 0.6664	0.9997 and 0.9287
Absorption correction	–	analytical	empiric psi-scan	empirical psi-scan
Data	1964	1044	4351	2243
Restraints/parameters	0/160	1/127	0/274	0/148
Goodness-of-fit on F^2	0.983	0.903	1.956	0.994
Final R $[I > 2\theta(I)]$	$R1 = 0.0380$, $wR2 = 0.0806$	$R1 = 0.0527$, $wR2 = 0.1201$	$R1 = 0.1443$, $wR2 = 0.4404$	$R1 = 0.0555$, $wR2 = 0.1560$
R Indices (all data)	$R1 = 0.0804$, $wR2 = 0.0968$	$R1 = 0.0990$, $wR2 = 0.1409$	$R1 = 0.1947$, $wR2 = 0.4736$	$R1 = 0.0890$, $wR2 = 0.1792$
Absolute structure parameter	–	0.0(2)	–	–
Extinction coefficient	–	–	–	–
Largest diff. peak and hole, eÅ^{-3}	0.184 and −0.205	0.313 and −0.301	2.946 and −1.572	0.671 and −0.688

stitution of either the electron donating or withdrawing groups in the benzene ring and in the side chain. In continuation of our efforts in this direction [4–6, 9, 11–17], we report now the crystal structures of *N*-(*meta*-substituted phenyl)-2,2,2-trichloro-acetamides of the general formulae 3-XC_6H_4NH-CO-CCl_3 and 3,5-$X_2C_6H_3NH$-CO-CCl_3 (X = Cl, CH_3), namely *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide, 3-CH_3-C_6H_4NH-CO-CCl_3 (**3MPTCA**); *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide, 3-ClC_6H_4NH-CO-CCl_3 (**3CPTCA**); *N*-(3,5-dimethylphenyl)-2,2,2-trichloro-acetamide, 3,5-$(CH_3)_2C_6H_3NH$-CO-CCl_3 (**35DMPTCA**) and *N*-(3,5-dichlorophenyl)-2,2,2-trichloro-acetamide, 3,5-$Cl_2C_6H_3NH$-CO-CCl_3 (**35DCPTCA**) at room temperature. The present data have been analyzed along with earlier crystal structures on *N*-(phenyl)-acetamide, C_6H_5NH-CO-CH_3 (**PA**) [18]; *N*-(phenyl)-2,2,2-trichloro-acetamide, C_6H_5NH-CO-CCl_3 (**PTCA**) [4]; *N*-chloro-*N*-(phenyl)-2,2,2-trichloro-acetamide, C_6H_5NCl-CO-CCl_3 (**NCPTCA**) [4]; *N*-(3-nitrophenyl)-2,2,2-trichloro-acetamide, 3-$NO_2C_6H_4NH$-CO-CCl_3 (**3NPTCA**) [9], and

Table 2. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters ($Å^2 \cdot 10^3$) of *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-CCl_3; *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide, 3-ClC_6H_4NH-CO-CCl_3; *N*-(3,5-dimethylphenyl)-2,2,2-trichloro-acetamide, 3,5-$(CH_3)_2C_6H_3NH$-CO-CCl_3 and *N*-(3,5-dichlorophenyl)-2,2,2-trichloro-acetamide, 3,5-$Cl_2C_6H_3NH$-CO-CCl_3. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)
3-$CH_3C_6H_4NH$-CO-CCl_3				
Cl(1)	5738(8)	4446(7)	5739(4)	104(2)
Cl(1D)	5479(9)	4216(12)	5831(4)	105(2)
Cl(2)	5171(1)	1835(10)	5020(6)	109(3)
Cl(2D)	5331(9)	1834(10)	4909(5)	73(2)
Cl(3)	7217(6)	3283(14)	4807(4)	123(3)
Cl(3D)	7140(6)	3701(17)	4865(4)	106(3)
C(4)	6218(2)	2838(3)	5395(1)	55(1)
C(5)	6778(2)	1846(3)	5924(1)	41(1)
O(6)	6478(1)	577(2)	6007(1)	50(1)
N(7)	7555(2)	2539(2)	6260(1)	48(1)
C(8)	8128(2)	1983(2)	6818(1)	43(1)
C(9)	7681(2)	962(2)	7252(1)	45(1)
C(10)	8241(2)	526(3)	7815(1)	52(1)
C(11)	9250(3)	1123(3)	7930(2)	71(1)
C(12)	9695(2)	2135(4)	7499(2)	81(1)
C(13)	9146(2)	2568(3)	6939(2)	61(1)
C(14)	7739(3)	−556(3)	8293(1)	77(1)
3-ClC_6H_4NH-CO-CCl_3				
C(8)	269(4)	1703(2)	−3521(15)	44(2)
C(13)	−136(5)	1779(2)	−5502(19)	65(3)
C(12)	22(7)	2055(3)	−6812(18)	79(3)
C(11)	542(6)	2257(2)	−6146(19)	72(3)
C(10)	913(5)	2183(2)	−4200(20)	65(3)
C(9)	789(5)	1907(2)	−2854(15)	52(2)
C(5)	589(5)	1225(2)	−1223(15)	49(2)
C(4)	307(5)	915(2)	39(15)	50(2)
N(7)	102(4)	1414(1)	−2241(12)	47(2)
O(6)	1196(3)	1277(1)	−1225(12)	69(2)
Cl(14)	1603(2)	2432(1)	−3394(9)	132(2)
Cl(2)	913(2)	774(1)	2085(6)	121(1)
Cl(3)	−469(2)	977(1)	1548(6)	97(1)
Cl(1)	171(3)	616(1)	−2141(6)	124(2)

ortho-/*para*-substituted *N*-phenyl-2,2,2-trichloro-acetamides [6, 9, 19], such as *N*-(2-methylphenyl)-2,2,2-trichloro-acetamide, 2-$CH_3C_6H_4NH$-CO-CCl_3 (**2MPTCA**) [19]; *N*-(2-chlorophenyl)-2,2,2-trichloro-acetamide, 2-ClC_6H_4NH-CO-CCl_3 (**2CPTCA**) [9]; *N*-(2-nitrophenyl)-2,2,2-trichloro-acetamide, 2-NO_2-C_6H_4NH-CO-CCl_3 (**2NPTCA**); *N*-(4-methylphenyl)-2,2,2-trichloro-acetamide, 4-$CH_3C_6H_4NH$-CO-CCl_3 (**4MPTCA**) [6]; *N*-(4-chlorophenyl)-2,2,2-trichloro-acetamide, 4-ClC_6H_4NH-CO-CCl_3 (**4CPTCA**) and *N*-(4-nitrophenyl)-2,2,2-trichloro-acetamide, 4-$NO_2C_6H_4NH$-CO-CCl_3 (**4NPTCA**) [9].

Table 2 (continued).

Atom	*x*	*y*	*z*	*U*(eq)
3,5-$(CH_3)_2C_6H_3NH$-CO-CCl_3				
C(4)	−3251(10)	5243(12)	1083(6)	64(3)
C(5)	−2661(8)	6040(9)	1725(5)	43(2)
C(8)	−3555(7)	7224(7)	3106(5)	34(2)
C(9)	−2479(8)	8218(9)	2821(6)	46(2)
C(10)	−2335(8)	9022(9)	3479(6)	48(2)
C(11)	−3283(9)	8770(8)	4398(6)	46(2)
C(12)	−4365(9)	7752(8)	4708(6)	45(2)
C(13)	−4509(8)	6948(8)	4038(5)	41(2)
C(14)	−1173(11)	10162(10)	3155(8)	69(3)
C(15)	−5367(11)	7451(10)	5729(6)	62(2)
C(19)	667(9)	4186(9)	3430(7)	52(2)
C(20)	1722(8)	5443(8)	3069(6)	44(2)
C(23)	1906(8)	7703(8)	2041(6)	42(2)
C(24)	2646(9)	8369(8)	2536(6)	47(2)
C(25)	3255(9)	9642(9)	2121(7)	53(2)
C(26)	3170(10)	10205(10)	1210(7)	64(3)
C(27)	2455(10)	9584(10)	709(7)	61(2)
C(28)	1816(9)	8270(9)	1152(6)	48(2)
C(29)	4033(13)	10396(10)	2661(10)	77(3)
C(30)	2352(16)	10177(13)	−281(9)	93(4)
N(7)	−3794(7)	6422(8)	2448(5)	45(2)
N(22)	1214(7)	6414(7)	2457(5)	50(2)
O(6)	−1303(6)	6268(7)	1524(4)	61(2)
O(21)	2861(6)	5500(6)	3310(4)	58(2)
Cl(1)	−4919(4)	6159(7)	794(3)	168(3)
Cl(2)	−3889(13)	3750(6)	1661(3)	278(6)
Cl(3)	−1946(4)	5265(6)	−1(2)	130(2)
Cl(16)	−1255(3)	4659(4)	3924(3)	111(1)
Cl(17)	821(6)	3348(4)	2455(3)	122(2)
Cl(18)	1288(4)	3045(3)	4286(3)	94(1)
3,5-$Cl_2C_6H_3NH$-CO-CCl_3				
C(4)	7044(2)	−3838(4)	4145(4)	56(1)
C(5)	6622(2)	−2831(4)	3571(4)	42(1)
C(8)	6053(2)	−997(4)	4254(4)	39(1)
C(9)	5652(2)	−940(4)	3194(4)	46(1)
C(10)	5321(2)	133(5)	3050(4)	52(1)
C(11)	5372(2)	1134(4)	3888(5)	56(1)
C(12)	5772(2)	1043(4)	4921(4)	50(1)
C(13)	6111(2)	−6(4)	5124(4)	43(1)
N(7)	6411(2)	−2044(4)	4490(3)	46(1)
O(6)	6499(2)	−2829(3)	2403(3)	58(1)
Cl(1)	6612(1)	−4878(2)	5115(2)	100(1)
Cl(2)	7389(1)	−4640(2)	2865(2)	131(1)
Cl(3)	7582(1)	−3162(1)	5192(2)	81(1)
Cl(14)	4808(1)	188(2)	1756(1)	81(1)
Cl(15)	5856(1)	2287(1)	6009(2)	82(1)

2. Experimental

2.1. Preparation and Characterization of the Compounds

The compounds *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide (**3MPTCA**); *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide (**3CPTCA**); *N*-(3,5-dimethylphenyl)-2,2,2-trichloro-acetamide (**35DMPTCA**)

Table 3. Comparison of crystal structure data of *N*-(substituted-phenyl)-2,2,2-trichloro-acetamides.

Parameter	**PA**	**PTCA**	**NCPTCA**	**2MPTCA**	**2CPTCA**	**2NPTCA**	**3MPTCA**	**3CPTCA**	**3NPTCA**	**4MPTCA**	**4CPTCA**	**4NPTCA**	**35DMPTCA**	**35DCPTCA**
Crystal system	ortho-rhombic	mono-clinic	mono-clinic	ortho-rhombic	ortho-rhombic	tri-clinic	ortho-rhombic	ortho-rhombic	tri-clinic	mono-clinic	ortho-rhombic	mono-clinic	tri clinic	ortho-rhombic
Space group	*Pbca*	$P2_1c$	$P2_1c$	$P2_12_12_1$	$Pna2_1$	$P\bar{1}$	*Pbca*	*Fdd*2	$P\bar{1}$	$P2_1/c$	*Pbca*	$P2_1/n$	$P\bar{1}$	*Pbca*
Z	8	4	4	4	4	4	8	16	4	8	8	4	2	8
Bond lengths, Å:														
C(ring)-C(ring), mean	1.387	1.383	1.377	1.377	1.383	1.385	1.378	1.364	1.381	1.381	1.378	1.383	1.383	1.379
min.	1.366	1.373	1.365	1.363	1.368	1.371	1.371	1.335	1.373	1.375	1.368	1.366	1.354	1.368
max.	1.413	1.390	1.386	1.394	1.391	1.404	1.387	1.391	1.391	1.391	1.387	1.397	1.431	1.395
C(ring)-N	1.426	1.424	1.443	1.427	1.420	1.402	1.421	1.414	1.414	1.427	1.416	1.415	1.427	1.402
N-C(O)	1.330	1.337	1.346	1.320	1.340	1.344	1.328	1.342	1.340	1.336	1.328	1.343	1.347	1.337
C-O	1.226	1.211	1.200	1.217	1.207	1.195	1.209	1.189	1.206	1.217	1.210	1.195	1.191	1.204
C(O)-C(side)	1.476	1.564	1.562	1.531	1.561	1.562	1.552	1.548	1.559	1.550	1.555	1.571	1.550	1.549
C(side)-Cl(1)	–	1.768	1.759	1.748	1.758	1.755	1.739	1.744	1.765	1.761	1.764	1.756	1.785	1.771
C(side)-Cl(2)	–	1.762	1.770	1.754	1.769	1.761	1.735	1.732	1.764	1.763	1.767	1.773	1.693	1.729
C(side)-Cl(3)	–	1.772	1.764	1.753	1.770	1.757	1.751	1.737	1.754	1.770	1.743	1.762	1.712	1.759
Bond angles, deg.:														
C(2r)-C(1r)-C(6r)	121.2	119.9	121.5	121.1	119.0	117.0	120.1	120.0	119.9	119.4	119.6	120.0	121.5	120.5
C(2r)-C(1r)-N	115.7	122.1	119.6	119.7	119.9	121.2	122.5	122.6	122.9	119.4	122.2	117.6	121.2	122.3
C(6r)-C(1r)-N	122.7	117.9	118.8	119.2	121.1	121.8	117.3	117.4	117.2	121.2	118.1	122.4	117.4	117.2
C(1r)-N-C(O)	129.3	125.4	132.3	123.7	122.4	127.9	126.9	122.2	126.3	124.1	125.6	126.6	125.0	126.4
N-C(O)-C(side)	117.7	114.8	118.6	115.2	114.1	113.8	113.8	114.7	114.2	116.5	114.4	113.7	113.3	113.8
N-C(O)-O	121.7	126.3	123.0	125.6	125.8	127.4	126.2	126.0	125.1	125.3	126.0	126.5	126.5	126.0
O-C(O)-C(side)	120.4	118.9	118.3	119.2	120.1	118.9	120.0	119.3	120.8	118.2	119.6	119.7	120.2	120.2
C(O)-C(side)-Cl(1)	–	113.4	116.1	D	110.7	112.7	D	107.8	109.4	111.5	109.5	109.1	109.6	108.0
C(O)-C(side)-Cl(2)	–	110.0	106.8	I	108.9	107.5	I	109.6	109.2	108.8	108.6	108.3	109.8	110.3
C(O)-C(side)-Cl(3)	–	106.9	107.9	S	109.4	107.5	S	113.9	110.0	106.9	110.9	111.7	111.1	110.7
Cl(1)-C(side)-Cl(2)	–	108.4	109.5	O	109.0	108.7	O	109.4	109.5	108.5	109.3	108.7	108.2	109.9
Cl(1)-C(side)-Cl(3)	–	109.5	107.4	R	108.3	109.1	R	108.2	109.4	109.0	108.9	109.7	106.3	108.0
Cl(2)-C(side)-Cl(3)	–	108.6	109.0	DER	110.5	109.9	DER	108.0	109.4	109.1	109.7	109.4	111.5	109.9

Table 4. Comparison of selected dihedral angles (degree) (standard deviations) of some *N*-(substituted-phenyl)-2,2,2-trichloro-acetamides.

Connection	Dihedral angle							
	3MPTCA	**3CPTCA**	**35DMPTCA**		**35DCPTCA**	**2MPTCA**	**2CPTCA**	**4NPTCA**
			Molecule 1	Molecule 2				
Cl(1)-C(s)-C(o)-O	124.3(4)	−98.4(9)	−131.7(8)	127.3(8)	−108.0(4)	−20.0(8)	1.4(3)	14.5(4)
Cl(2)-C(s)-C(o)-O	1.6(5)	20.6(1)	112.5(9)	−111.1(8)	12.1(6)	98.1(7)	−118.5(2)	135.8(3)
Cl(3)-C(s)-C(o)-O	−117.2(4)	141.6(8)	−18.5(1)	6.0(1)	133.9(4)	−143.4(7)	120.7(2)	−103.6(3)
Cl(1)-C(s)-C(o)-N	−54.3(5)	81.5(7)	46.9(9)	−53.7(9)	69.9(4)	161.6(6)	−177.7(2)	−167.0(2)
Cl(2)-C(s)-C(o)-N	−176.9(5)	−159.5(6)	−68.9(1)	67.9(8)	−170.1(3)	−80.4(7)	62.4(2)	−45.6(3)
Cl(3)-C(s)-C(o)-N	64.3(5)	−38.5(9)	160.1(7)	−175.0(6)	−48.2(5)	38.3(7)	−58.4(2)	74.9(3)
C(s)-C(o)-N-C(1r)	172.7(2)	−178.4(7)	−176.7(8)	177.2(7)	175.6(4)	175.8(5)	−179.9(2)	−174.8(2)
C(o)-N-C(1r)-C(2r)	−28.0(4)	−36.8(1)	35.1(1)	−32.3(1)	30.6(7)	−57.4(8)	−135.2(2)	−163.0(3)
C(o)-N-C(1r)-C(6r)	155.6(2)	144.8(8)	−146.4(8)	148.2(8)	−149.5(4)	123.9(6)	45.1(3)	18.3(4)
O-C(o)-N-C(1r)	−5.7(4)	1.4(1)	1.7(1)	−3.8(1)	−6.7(7)	−2.5(10)	1.0(3)	3.6(5)
N-C(1r)-C(2r)-C(3r)	−175.6(2)	−179.8(7)	176.9(7)	−177.7(7)	180.0(4)	−178.0(5)	−179.4(2)	−178.3(2)
N-C(1r)-C(6r)-C(5r)	175.6(3)	−178.7(8)	−177.3(7)	178.3(7)	179.4(4)	178.5(5)	−179.8(2)	177.7(3)
N-C(1r)-C(2r)-C(me)/Cl/N(1)	–	–	–	–	–	0.2(8)	0.8(3)	–
C(6r)-C(1r)-C(2r)-C(me)/Cl/N(1)	–	–	–	–	–	−178.5(6)	−179.5(2)	–
C(4r)-C(3r)-C(2r)-C(me)/Cl/N(1)	–	–	–	–	–	178.0(6)	179.3(2)	–
C(1r)-C(2r)-C(3r)-C(me)/Cl/N(1)	178.5(2)	−177.4(8)	−178.0(8)	178.6(8)	−178.3(3)	–	–	–
C(1r)-C(6r)-C(5r)-C(me)/Cl/N(2)	–	–	−178.8(8)	179.3(1)	−179.2(3)	–	–	–
C(5r)-C(4r)-C(3r)-C(me)/Cl/N(1)	−178.6(3)	177.5(9)	179.1(8)	−178.4(9)	178.3(3)	–	–	–
C(3r)-C(4r)-C(5r)-C(me)/Cl/N(2)	–	–	177.9(8)	−179.9(1)	179.8(3)	–	–	–
C(6r)-C(5r)-C(4r)-C(me)/Cl/N	–	–	–	–	–	–	–	−179.7(2)
C(2r)-C(3r)-C(4r)-C(me)/Cl/N	–	–	–	–	–	–	–	179.2(2)

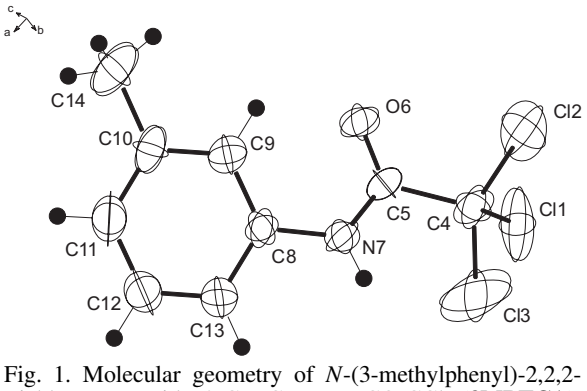

Fig. 1. Molecular geometry of *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-CCl_3 (**3MPTCA**), with the numbering of atoms. Displacement ellipsoids are drawn at the 50% probability level.

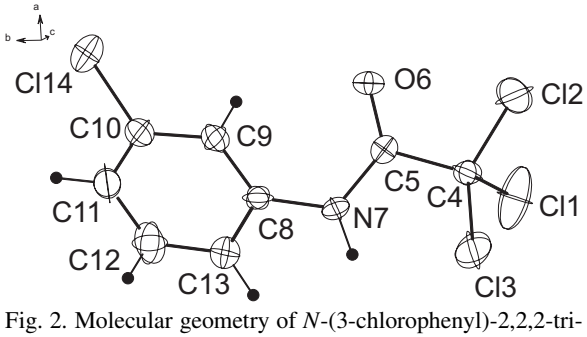

Fig. 2. Molecular geometry of *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide, 3-ClC_6H_4NH-CO-CCl_3 (**3CPTCA**), with the numbering of atoms. Displacement ellipsoids are drawn at the 50% probability level.

and *N*-(3,5-dichlorophenyl)-2,2,2-trichloro-acetamide (**35DCPTCA**) were prepared from the corresponding *meta*-methyl/chloro- or 3,5-dimethyl/dichloroanilines, trichloro-acetic acid and phosphoryl chloride (Aldrich, Germany) [7, 20, 21]. The commercial solid anilines were purified by zone refining. The liquids were purified by double distillations. All other reagents employed in the preparation and purification of the compounds were of analytical grade.

The amides **3MPTCA**, **3CPTCA**, **35DMPTCA** and **35DCPTCA** were prepared, respectively, by treating 3-methylaniline (*m*-toluidine), 3-chloroaniline, 3,5-dimethylaniline and 3,5-dichloroaniline with a clear mixture of trichloroacetic acid and phosphoryl chloride under constant stirring. The mixtures were slowly warmed to expel HCl. Excess phosphoryl chloride was hydrolyzed by adding cold water dropwise under ice-cold conditions. The solids were filtered under suction, washed thoroughly with water and dried. The amides were recrystallized from ethanol several times. The purity of the compounds was checked by elemental analysis (C, H and N) and by determining their melting points. The compounds **3MPTCA**, **3CPTCA**, **35DMPTCA** and **35DCPTCA** were further charac-

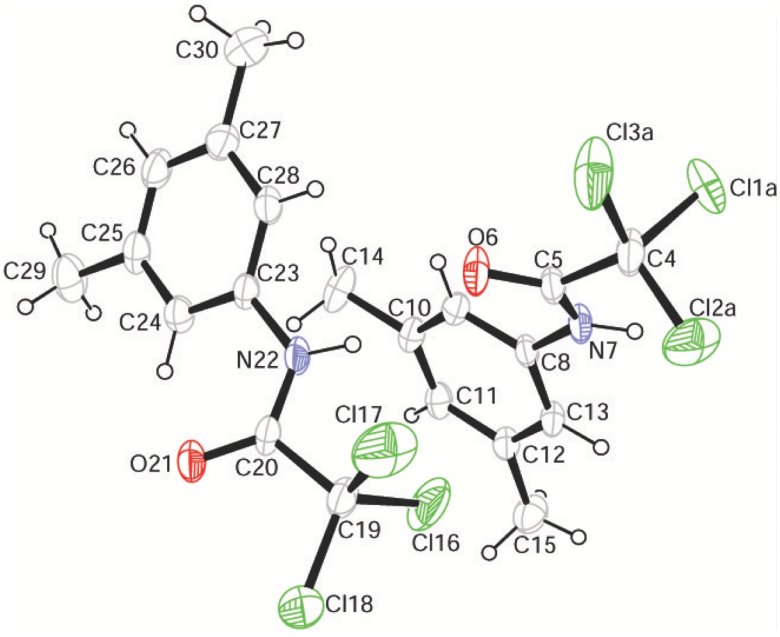

Fig. 3. Molecular geometry of *N*-(3,5-dimethylphenyl) - 2,2,2 - trichloro-acetamide, 3,5-$(CH_3)_2C_6H_3NH$-CO-CCl_3 (**35DMPTCA**), with the numbering of atoms. Displacement ellipsoids are drawn at the 50% probability level.

terized by recording their infrared and ^{35}Cl NQR spectra.

2.2. X-Ray Diffraction Studies

Small single crystals of **3MPTCA**, **3CPTCA**, **35DMPTCA** and **35DCPTCA** were selected for X-ray diffraction and studied at room temperature. The collected intensity data were corrected for Lorentz polarisation and absorption. The crystal structures were solved by direct methods and least squares refinement (SHELXL-97) [22 – 32]. 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. Further experimental conditions for structure determinations and refinements are given in Table 1.

3. Results and Discussion

The crystallographic data for the amides **3MPTCA**, **3CPTCA**, **35DMPTCA** and **35DCPTCA** are shown in Table 1. The atomic coordinates and the mean displacement parameters are listed in Table 2. The intramolecular bond distances and angles of these amides and other related compounds are compared in Table 3, while Table 4 compares the selected dihedral angles for this class of compounds. The hydrogen

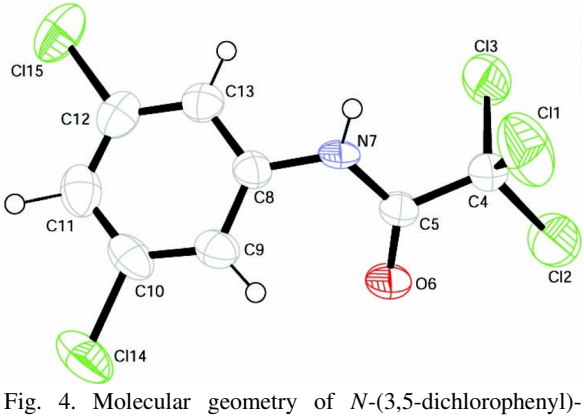

Fig. 4. Molecular geometry of *N*-(3,5-dichlorophenyl)-2,2,2-trichloro-acetamide, 3,5-$Cl_2C_6H_3NH$-CO-CCl_3 (**35DCPTCA**), with the numbering of atoms. Displacement ellipsoids are drawn at the 50% probability level.

coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations of these compounds have been deposited at the Cambridge Crystallographic Data Centre [CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk)]. The CCDC numbers are 611445, 240069, 608782 and 240068, respectively, for *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-CCl_3 (**3MPTCA**); *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide, 3-Cl-C_6H_4NH-CO-CCl_3 (**3CPTCA**); *N*-(3,5-dimethyl-

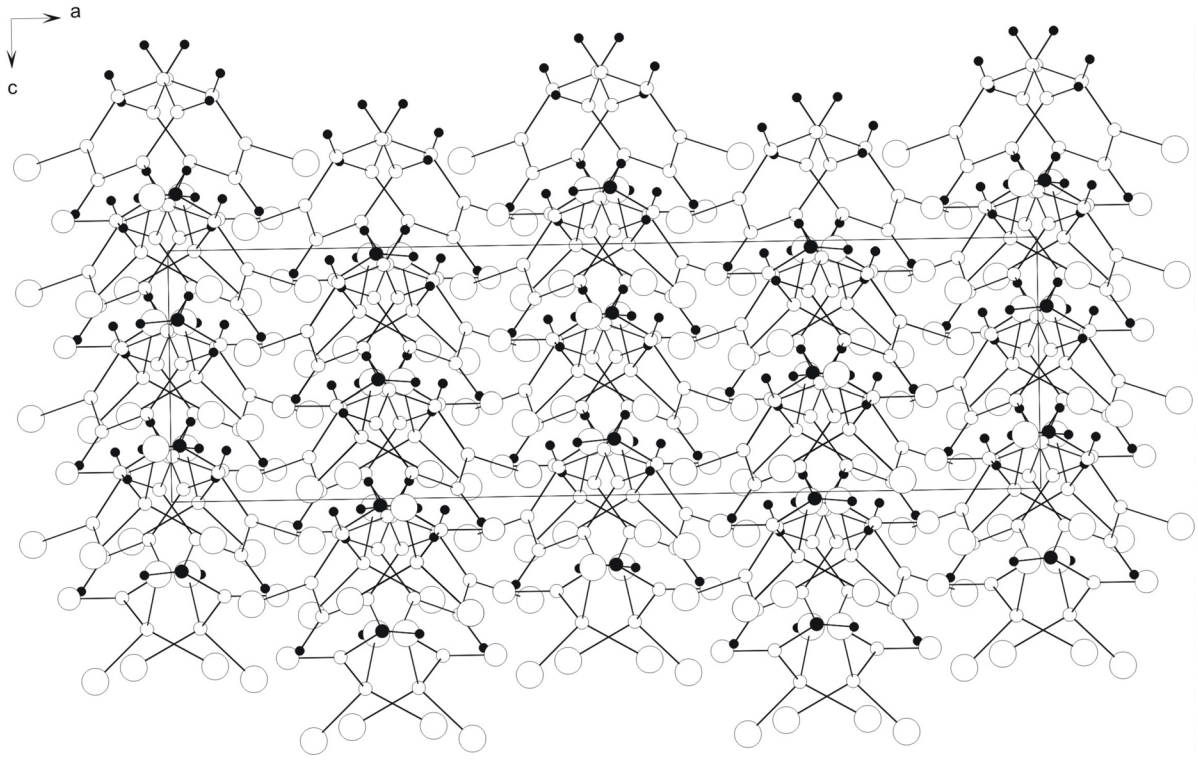

Fig. 5. Projection of the unit cell of 3-ClC_6H_4NH-CO-CCl_3 (**3CPTCA**).

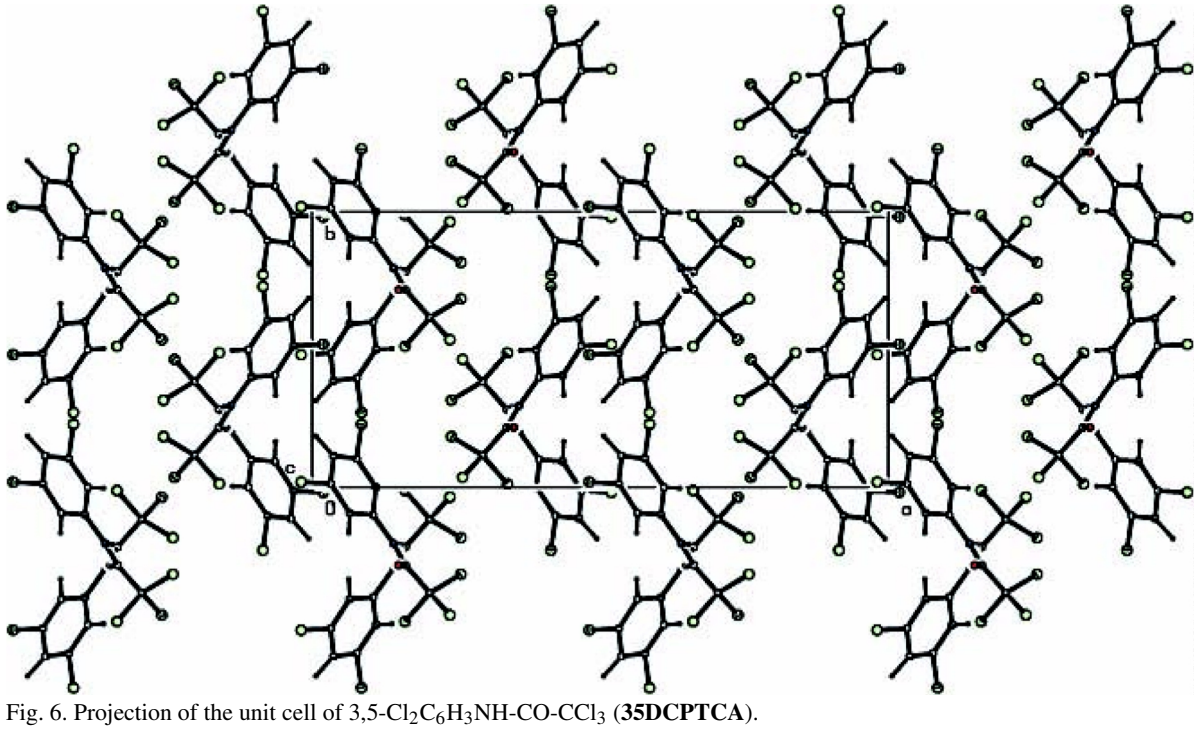

Fig. 6. Projection of the unit cell of 3,5-$Cl_2C_6H_3NH$-CO-CCl_3 (**35DCPTCA**).

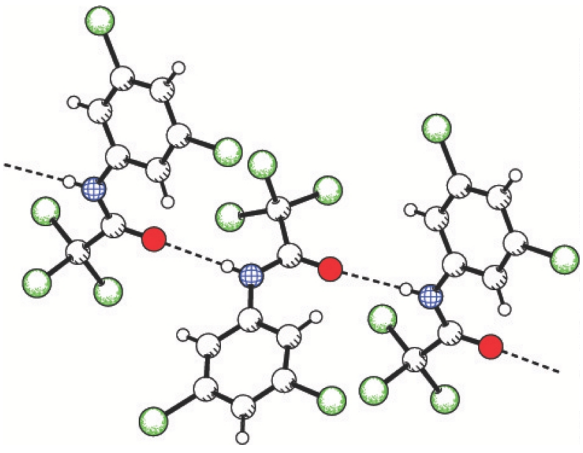

Fig. 7. Typical hydrogen bond bridges observed in the structure of 3,5-$Cl_2C_6H_3NH$-CO-CCl_3 (**35DCPTCA**).

phenyl)-2,2,2-trichloro-acetamide, 3,5-$(CH_3)_2C_6H_3$-NH-CO-CCl_3 (**35DMPTCA**) and *N*-(3,5-dichlorophenyl)-2,2,2-trichloro-acetamide, 3,5-$Cl_2C_6H_3NH$-CO-CCl_3 (**35DCPTCA**). Figures 1, 2, 3 and 4 show the molecules of the title compounds as they appear in suitable projection with the numbering of the atoms used throughout the paper. The displacement ellipsoids are drawn at 50% probability level. The projection of the typical unit cells of a mono- and a disubstituted compound, **3CPTCA** and **35DCPTCA**, are shown in Figs. 5 and 6, respectively. Typical hydrogen bond bridges in **35DCPTCA** are shown in Figure 7.

The compound **35DMPTCA** has two molecules in its asymmetric unit, similar to that observed in the asymmetric units of the compounds **4MPTCA, 2NPTCA** and **3NPTCA**, while the compounds **3MPTCA**, **3CPTCA** and **35DCPTCA** have one molecule each in their asymmetric units, similar to the amides, **PA**, **PTCA**, **NCPTCA**, **2MPTCA**, **2CPTCA**, **4CPTCA** and **4NPTCA**. This agrees with the observed ^{35}Cl NQR spectra of the compounds.

It is evident from the analysis of the crystal structure data of aryl-2,2,2-trichloro-acetamides in Table 3, that **2NPTCA**, **3NPTCA** and **35DMPTCA** crystallize in triclinic symmetry, while the other amides crystallize either in orthorhombic or monoclinic symmetry. With the exception of **4MPTCA**, aryl-2,22-trichloro-acetamides which crystallize in triclinic symmetry have 2 molecules each in their asymmetric units, while other trichloroamides, which crystallize either in orthorhombic or monoclinic symmetry, have one molecule each in their asymmetric units. The *N*-chlorination of **PTCA** has no effect on the crystal system, space group or *Z* number. But the introduction of different groups at various positions in the benzene ring has varying effects, the generalization of which requires extensive further work in this direction. In general, the introduction of electron withdrawing or electron donating substituents either at a side chain or in the benzene ring changes the crystal characteristic parameters, unless the substituent effect is marginal or is compensated by the opposite substitution. Introduction of Cl atom to the phenyl group in **PTCA** either at *ortho*, *meta*, *para* or at both the *meta* positions changes the crystal symmetry from monoclinic to orthorhombic but with different space groups and *Z* numbers. The introduction of a methyl or nitro group at the *para* position away from the bulky side chain has no effect on the crystal system, while the introduction of the methyl group either at the *ortho* or *meta* position of **PTCA** changes the crystal system from monoclinic to orthorhombic with different space groups and *Z* numbers. The introduction of methyl groups at both *meta* positions changes the crystal system from monoclinic to triclinic. But the introduction of a nitro group to **PTCA** either at an *ortho* or the *meta* position itself changes the crystal symmetry from monoclinic to triclinic. The nitro-substitutions at *ortho* or *meta* positions will have a more pronounced effect on the crystal geometry of the amides than the other groups at these positions and substitutions at the *para* positions.

However it is premature to generalize these aspects, unless extensive work is carried out with varying substitutions in both the benzene ring and in the side chain in terms of the nature and the number of substituents. Work in this direction is in progress.

The mean ring distances, along with the observed minimum and maximum distances and other bond distances for 15 unsubstituted and substituted amides are compared in Table 3. The minimum and maximum mean ring distances are observed at 1.364 Å and 1.387 Å for **3CPTCA** and **PA**, respectively. The longest ring distance is observed at 1.431 Å for **35DMPTCA**, which is dimethyl *meta*-substituted, while the shortest ring distance is observed at 1.335 Å **3CPTCA**, which is also a *meta*-substituted amide. The ring mean distance is also the minimum for this amide.

The minimum and maximum C(ring)-N distances are observed at 1.402 Å (**2NPTCA** and **35DCPTCA**) and 1.443 Å (**NCPTCA**), respectively. The *N*-chlorination of **PTCA** increases the C(ring)-N distance by 0.019 Å, while the mono-nitro-substitution at the *ortho* position or the di-*meta*-chloro-substitution in

PTCA decreases the C(ring)-N distance by 0.022 Å. The ring methyl-substitutions have no significant effect, while the other ring substitutions shorten the C(ring)-N distance. But the ring methyl-substitutions shorten the *N*-C(O) distance, the effect of *para*-substitution being negligible. But the di-*meta*-methyl-substitutions increase this distance. The maximum and minimum distances are observed at 1.320 Å and 1.347 Å for **2NPTCA** and **35DMPTCA**, respectively. The minimum and maximum C-O distances are observed at 1.189 Å and 1.226 Å for **3CPTCA** and **PA**, respectively, while the minimum and maximum C(O)-C(side) bond lengths are observed at 1.476 Å and 1.571 Å for **PA** and **4NPTCA**, respectively.

As regards the bond angles, the minimum and maximum C(2r)-C(1r)-C(6r) bond angles occur at 117.0° and 121.5° for **2NPTCA** and **35DMPTCA** for **NCPTCA**, respectively, while both the minimum and maximum C(2r)-C(1r)-N and C(6r)-C(1r)-N bond angles are observed for **PA** at 115.7° and 122.7°. The minimum and maximum bond angles of C(1r)-*N*-C(O), *N*-C(O)-C(side), *N*-C(O)-O and O-C(O)-C(side) are observed, respectively, at 122.2° (**3CPTCA**) and 132.3° (**NCPTCA**); 113.3° (**35DMPTCA**) and 118.6° (**NCPTCA**); 121.7° (**PA**) and 127.4° (**2NPTCA**); 118.2° (**4MPTCA**) and 120.8° (**3NPTCA**). The other side chain angles are also affected on substitution in the ring, depending on the site and the nature of substitution.

The comparison of available significant dihedral angles for the compounds are shown in Table 4. It is evident from the data that with the same group in the side chain, the dihedral angles C(s)-C(o)-*N*-C(1r) are higher by about 1.9 to 5.7° for the ring chloro-substituted compounds than the ring methyl-substituted compounds. As may be seen, the other dihedral angles also undergo changes to different extents, depending on the nature of the substituent and the position of the substitution.

The comparison of the geometrical parameters revealed that there are significant changes in them, with substitution in the benzene ring keeping the side chain the same. But, as already indicated, to draw general conclusions, further substantive data are to be collected with varying substitutions. Our work in this direction is in progress.

Acknowledgements

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