Effect of Substituent on Crystal Structures of N-(Substituted-phenyl)-2,2,2-Trichloroacetamides, 2/3/4-XC_6H_4.NHCO.CCl_3 (X = Cl, NO_2 or CH_3)

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The crystal structures of N-(substitutedphenyl)-2,2,2-trichloroacetamides of the type 2/3/4-XC_6H_4.NHCO.CCl_3 (X = Cl, NO_2 or CH_3), namely, N-(3-nitrophenyl)-2,2,2-trichloroacetamide, 3-$NO_2C_6H_4$.NHCO.CCl_3 (**m-NO_2PhTCA**); N-(4-nitrophenyl)-2,2,2-trichloroacetamide, 4-$NO_2C_6H_4$.NHCO.CCl_3 (**p-NO_2PhTCA**); N-(2-chlorophenyl)-2,2,2-trichloroacetamide, 2-ClC_6H_4.NHCO.CCl_3 (**o-ClPhTCA**) and N-(4-chlorophenyl)-2,2,2-trichloroacetamide, 4-ClC_6H_4.NHCO.CCl_3 (**p-ClPhTCA**) have been determined at room temperature. The present data are analysed along with our earlier crystal structures of N-(2-nitrophenyl)-2,2,2-trichloroacetamide, 2-$NO_2C_6H_4$.NHCO.CCl_3 (**o-NO_2PhTCA**); N-(4-methylphenyl)-2,2,2-trichloroacetamide, 4-$CH_3C_6H_4$. NHCO.CCl_3 (**p-CH_3PhTCA**); N-(phenyl)-2,2,2-trichloroacetamide, C_6H_5.NHCO.CCl_3 (**PhTCA**); N-chloro-N-(phenyl)-2,2,2-trichloroacetamide, C_6H_5.NClCO.CCl_3 (**NClPhTCA**); and finally with N-(phenyl) acetamide, C_6H_5.NHCO.CH_3 (**PhA**). The crystal type, space group, formula units and lattice constants in Å of the new structures are; **m-NO_2PhTCA**: triclinic, P$\bar{1}$, $Z = 4$, $a = 7.493(3)$, $b = 9.992(3)$, $c = 15.225(5)$, $\alpha = 84.16(2)°$, $\beta = 82.59(2)°$, $\gamma = 84.92(2)$; **p-NO_2PhTCA**: monoclinic, $P2_1/n$, $Z = 4$, $a = 5.807(2)$, $b = 15.354(6)$, $c = 12.475(5)$, $\beta = 92.28(2)°$; **o-ClPhTCA**: orthorhombic, $Pna2_1$, $Z = 4$, $a = 8.769(2)$, $b = 12.838(3)$, $c = 9.578(2)$ and **p-ClPhTCA**: orthorhombic, Pbca, $Z = 8$, $a = 9.742(4)$, $b = 10.031(4)$, $c = 23.110(9)$. The compounds, **m-NO_2PhTCA**, **o-NO_2PhTCA** and **p-CH_3PhTCA** show two molecules each in their asymmetric units. This is in agreement with the multiple lines observed in the ^{35}Cl NQR spectra of the latter two compounds. But the presence of two molecules in the asymmetric unit of **m-NO_2PhTCA** indicates that it may undergoe a phase transition below room temperature. The bond lengths and bond angles are normal except for some deviations. The presence of strong electron withdrawing group at the ortho position of the phenyl ring and N-chlorination of the amide will have significant effect on some bond distances and bond angles.

Key words: Substituent Effect; Crystal Structures; N-phenyltrichloroacetamides.

Introduction

Nuclear quadrupole resonance and crystal structure studies give valuable information on bond properties. NQR spectroscopy and XRD have extensively been used to investigate the structural aspects of a variety of compounds including amides [1 - 9]. We are interested in the structural studies of amides in their crystalline state using this combined tool [6 - 12]. 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 [13]. Thus the amide moiety is an important constituent of many biologically significant compounds [14]. Many amides exhibit pharmacological activity, which has further stimulated interest in their chemistry. Many acetanilides also exhibit fungicidal and herbicidal activities [15 - 17].

We have recently prepared several substituted amides of the configuration: $X_yC_6H_{5-y}$.

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Table 1. Experimental conditions for the crystal structure determination and crystallographic data of 3-$NO_2C_6H_4$.NHCO.CCl_3 (**m-NO_2PhTCA**); 4-$NO_2C_6H_4$.NHCO.CCl_3 (**p-NO_2PhTCA**); 2-ClC_6H_4.NHCO.CCl_3 (**o-ClPhTCA**) and 4-ClC_6H_4.NHCO.CCl_3 (**p-ClPhTCA**). Diffractometer: Stoe-Stadi 4; Monochromator: Graphite (002); scan 2 θ/ω; Refinement method: Full-matrix least-squares on F^2.

Compound	m-NO_2PhTCA	p-NO_2PhTCA	o-ClPhTCA	p-ClPhTCA
Chemical formula	$C_8H_5Cl_3N_2O_3$	$C_8H_5Cl_3N_2O_3$	$C_8H_5Cl_4NO$	$C_8H_5Cl_4NO$
Formula weight	283.49	283.49	272.93	272.93
Temperature, K	298(2)	299(2)	300(2)	297(2)
Wavelength, pm	71.073	71.073	71.069	71.073
Crystal system	triclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	$P\,2_1/n$	$Pna2_1$	Pbca
a, Å	7.493(3)	5.807(2)	8.769(2)	9.742(4)
b, Å	9.992(3)	15.354(6)	12.838(3)	10.031(4)
c, Å	15.225(5)	12.475(5)	9.578(2)	23.110(9)
α, deg.	84.16(2)	90	90	90
β, deg.	82.59(2)	92.28(2)	90	90
γ, deg.	84.92(2)	90	90	90
Volume, Å^3	1121.2(7)	1111.4(7)	1078.3(4)	2258(2)
Z	4	4	4	8
D_{calcd}, g cm^{-3}	1.679	1.694	1.681	1.605
Abs. coeff., cm^{-1}	8.08	8.15	10.61	10.13
$F(000)$	568	568	544	1088
Crystal size, mm^3	0.60×0.40×0.25	1.20×0.27×0.24	1.40×0.18×0.15	1.70×0.22×0.22
θ range, deg.	2.05 to 27.49	2.10 to 27.54	2.65 to 29.98	1.76 to 27.49.
Index ranges	$-9\leq h\leq 2$, $-12\leq k\leq 12$, $-19\leq l\leq 19$	$0\leq h\leq 7$, $-19\leq k\leq 7$, $-16\leq l\leq 16$	$-12\leq h\leq 1$, $0\leq k\leq 18$, $-13\leq l\leq 13$	$-12\leq h\leq 2$, $0\leq k\leq 12$, $0\leq l\leq 29$
Reflections coll.	6674	4077	3978	3086
Independent refl.	5125	2562	3150	2585
[R(int)]	0.0207	0.0334	0.0171	0.0163
Absorption corr.	–	–	Numerical	–
Max.and min.transm.	–	–	0.880 and 0.829	–
Data	5122	2561	3147	2582
Restraints/parameters	0 / 296	0 / 149	1 / 131	0 / 131
Goodness-of-fit on F^2	1.065	1.047	1.054	1.044
Final $R[I > 2\sigma(I)]$	$R1 = 0.0543$, $wR2 = 0.1263$	$R1 = 0.0466$, $wR2 = 0.1227$	$R1 = 0.0290$, $wR2 = 0.0729$	$R1 = 0.0585$, $wR2 = 0.1419$
R indices (all data)	$R1 = 0.0721$, $wR2 = 0.1456$	$R1 = 0.0616$, $wR2 = 0.1394$	$R1 = 0.0351$, $wR2 = 0.0793$	$R1 = 0.0892$, $wR2 = 0.1737$
Abs. str. parameter	–	–	0.06(6)	–
Extinction coeff.	0.020(2)	0.041(4)	0.0029(9)	0.0135(12)
Largest diff. Peak and hole e$^-$ Å^3	0.543 and –0.532	0.369 and –0.443	0.316 and –0.315	0.442 and –0.353

$NHCOCH_{3-y}Cl_y$ (where X = CH_3, NO_2 or Br and y = 1, 2 or 3) and measured ^{35}Cl NQR and IR spectra [10 - 12, 18]. We have observed some interesting trends in these spectra. 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 noticed. For example, N-(3-chlorophenyl)-2-chloroacetamide did not show ^{35}Cl NQR, while N-(3-methylphenyl)-2-chloroacetamide showed two $^{35}Cl(\omega)$ resonances. Similarly, N-(2-methylphenyl)-2,2,2-trichloroacetamide, N-(3-methylphenyl)-2,2,2-trichloroacetamide and N-(4-methylphenyl)-2,2,2-trichloroacetamide 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 N-(4-bromophenyl)-2,2,2-trichloroacetamide showed only one $^{35}Cl(\omega)$ NQR frequency. The corresponding nitrosubstituted compounds, namely N-(2-nitrophenyl)-2,2,2-trichloroacetamide, N-(3-nitrophenyl)-2,2,2-trichloroacetamide and N-(4-nitrophenyl)-2,2,2-trichloroacetamide showed 6, 3, and 3 $^{35}Cl(\omega)$ NQR frequencies for the same 3 $Cl(\omega)$ atoms present in all the 3 compounds. Some

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)
3-$NO_2C_6H_4$.NHCO.CCl_3 (m-NO_2PhTCA)									
Cl(1)	227(2)	8383(1)	1603(1)	73(1)	Cl(2)	4100(1)	8531(1)	1202(1)	70(1)
Cl(3)	1719(2)	10927(1)	1043(1)	68(1)	C(4)	2055(5)	9359(3)	1659(2)	52(1)
C(5)	2224(4)	9565(3)	2646(2)	47(1)	O(6)	2176(4)	10684(2)	2885(2)	64(1)
N(7)	2492(4)	8415(3)	3161(2)	53(1)	C(8)	2988(4)	8305(3)	4034(2)	49(1)
C(9)	2504(4)	9302(3)	4605(2)	48(1)	C(10)	3103(4)	9114(3)	5428(2)	52(1)
C(11)	4151(5)	7983(4)	5711(3)	63(1)	C(12)	4600(6)	7005(4)	5129(3)	72(1)
C(13)	4039(5)	7152(4)	4298(3)	64(1)	N(14)	2602(4)	10173(3)	6039(2)	62(1)
O(15)	1655(5)	11156(3)	5800(2)	82(1)	O(16)	3188(6)	10030(4)	6752(2)	104(1)
Cl(17)	732(1)	3254(1)	4206(1)	71(1)	Cl(18)	–967(1)	3519(1)	2610(1)	77(1)
Cl(19)	–733(2)	5853(1)	3537(1)	87(1)	C(20)	367(4)	4319(3)	3237(2)	48(1)
C(21)	2232(4)	4572(3)	2691(2)	44(1)	O(22)	2808(4)	5669(2)	2617(2)	65(1)
N(23)	3097(4)	3476(2)	2349(2)	45(1)	C(24)	4705(4)	3434(3)	1754(2)	42(1)
C(25)	5393(4)	4572(3)	1282(2)	47(1)	C(26)	6895(4)	4384(3)	662(2)	50(1)
C(27)	7732(5)	3141(4)	493(2)	59(1)	C(28)	7065(5)	2027(4)	990(3)	62(1)
C(29)	5562(4)	2170(3)	1614(2)	51(1)	N(30)	7637(4)	5588(4)	157(2)	67(1)
O(31)	7322(5)	6661(3)	482(3)	103(1)	O(32)	8533(4)	5450(4)	–563(2)	87(1)
4-$NO_2C_6H_4$.NHCO.CCl_3 (p-NO_2PhTCA)									
Cl(1)	6634(2)	6864(1)	7775(1)	78(1)	Cl(2)	7155(2)	5304(1)	9027(1)	78(1)
Cl(3)	2728(1)	5745(1)	8044(1)	94(1)	C(4)	5728(5)	5777(2)	7887(2)	57(1)
C(5)	6440(5)	5259(2)	6867(2)	54(1)	O(6)	7806(4)	5567(1)	6283(2)	83(1)
N(7)	5426(4)	4476(2)	6763(2)	58(1)	C(8)	5862(4)	3839(2)	5977(2)	51(1)
C(9)	4239(5)	3180(2)	5817(2)	56(1)	C(10)	4579(5)	2532(2)	5090(2)	60(1)
C(11)	6587(5)	2540(2)	4527(2)	57(1)	C(12)	8217(5)	3188(2)	4658(2)	60(1)
C(13)	7857(5)	3846(2)	5386(2)	58(1)	N(14)	6987(6)	1844(2)	3758(2)	73(1)
O(15)	5407(6)	1365(2)	3482(2)	106(1)	O(16)	8948(6)	1773(2)	3422(2)	102(1)
2-ClC_6H_4.NHCO.CCl_3 (o-ClPhTCA)									
Cl(1)	651(1)	726(1)	6292(1)	61(1)	Cl(2)	–2020(1)	997(1)	4597(1)	65(1)
Cl(3)	–613(1)	2767(1)	5984(1)	65(1)	C(4)	–277(2)	1569(2)	5122(2)	41(1)
C(5)	728(2)	1765(1)	3803(2)	38(1)	O(6)	1949(2)	1339(2)	3688(2)	59(1)
N(7)	117(2)	2431(1)	2884(2)	43(1)	C(8)	860(2)	2706(2)	1618(2)	40(1)
C(9)	915(2)	3738(2)	1204(2)	42(1)	C(10)	1623(3)	4025(2)	–37(3)	56(1)
C(11)	2286(4)	3277(3)	–852(3)	70(1)	C(12)	2253(4)	2243(2)	–446(3)	69(1)
C(13)	1533(3)	1953(2)	777(3)	55(1)	Cl(14)	97(1)	4699(1)	2239(1)	62(1)
4-ClC_6H_4.NHCO.CCl_3 (p-ClPhTCA)									
Cl(1)	1631(2)	627(1)	2523(1)	88(1)	Cl(2)	13(1)	495(2)	1482(1)	94(1)
Cl(3)	400(2)	–1833(1)	2184(1)	99(1)	C(4)	1175(4)	–383(4)	1928(2)	59(1)
C(5)	2480(4)	–716(3)	1569(2)	48(1)	O(6)	2750(3)	–1866(2)	1459(1)	62(1)
N(7)	3204(3)	342(3)	1407(1)	50(1)	C(8)	4427(4)	313(3)	1076(2)	46(1)
C(9)	5375(4)	–705(4)	1126(2)	54(1)	C(10)	6573(4)	–658(4)	810(2)	60(1)
C(11)	6805(4)	386(4)	438(2)	56(1)	C(12)	5883(4)	1407(4)	384(2)	60(1)
C(13)	4690(4)	1370(4)	706(2)	56(1)	Cl(14)	8304(1)	406(1)	29(1)	85(1)

of the corresponding N-chloro compounds have also been prepared and their $^{35}Cl(N)$ and $^{35}Cl(\omega)$ NQR measured. Further, N-chloro-N-(3-chlorophenyl)-2-chloroacetamide showed all the three ^{35}Cl nuclear quadrupole resonances, while its N-H compound showed no ^{35}Cl(ring) and $^{35}Cl(\omega)$ NQR spectra. Similarly many of the compounds with the configuration: $C_6H_{5-y}Cl_y$-NCl-CO-CH_3 did not show $^{35}Cl(N)$ NQR, while those of $C_6H_{5-y}Cl_y$-NCl-CO-CH_2Cl showed $^{35}Cl(N)$ NQR spectra. Further, several of the compounds with the configuration: $(CH_3)_yC_6H_{5-y}Cl_y$-NCl-CO-CH_2Cl did not show ^{35}Cl NQR.

There are no reports on structural studies of these compounds to see how the -NHCO- bond parameters vary with the substitution both in the benzene ring and in the side chain. Hence we thought it interesting to make crystal structure studies of several of the above

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

Connection	Bond length	Connection	Bond length
m-NO_2PhTCA			
Cl(1)-C(4)	1.765(3)	Cl(17)-C(20)	1.765(3)
Cl(2)-C(4)	1.770(4)	Cl(18)-C(20)	1.758(3)
Cl(3)-C(4)	1.758(3)	Cl(19)-C(20)	1.749(3)
C(4)-C(5)	1.560(4)	C(20)-C(21)	1.558(4)
C(5)-O(6)	1.208(3)	C(21)-O(22)	1.203(4)
C(5)-N(7)	1.339(4)	C(21)-N(23)	1.340(4)
N(7)-C(8)	1.416(4)	N(23)-C(24)	1.411(4)
C(8)-C(9)	1.383(4)	C(24)-C(25)	1.384(4)
C(8)-C(13)	1.391(5)	C(24)-C(29)	1.389(4)
C(9)-C(10)	1.374(4)	C(25)-C(26)	1.385(4)
C(10)-C(11)	1.382(5)	C(26)-C(27)	1.374(5)
C(10)-N(14)	1.472(4)	C(26)-N(30)	1.472(4)
C(11)-C(12)	1.376(6)	C(27)-C(28)	1.375(5)
C(12)-C(13)	1.373(5)	C(28)-C(29)	1.383(5)
N(14)-O(15)	1.213(4)	N(30)-O(31)	1.218(5)
N(14)-O(16)	1.214(4)	N(30)-O(32)	1.222(4)
p-NO_2PhTCA		PhTCA	
Cl(1)-C(4)	1.756(3)	Cl(1)-C(4)	1.768(2)
Cl(2)-C(4)	1.773(3)	Cl(2)-C(4)	1.762(2)
Cl(3)-C(4)	1.762(3)	Cl(3)-C(4)	1.772(2)
C(4)-C(5)	1.571(4)	C(4)-C(5)	1.564(2)
C(5)-O(6)	1.195(3)	C(5)-O(6)	1.211(2)
C(5)-N(7)	1.343(3)	C(5)-N(7)	1.337(2)
N(7)-C(8)	1.415(3)	N(7)-C(8)	1.424(2)
C(8)-C(9)	1.392(3)	C(8)-C(9)	1.390(2)
C(8)-C(13)	1.397(3)	C(8)-C(13)	1.386(2)
C(9)-C(10)	1.366(4)	C(9)-C(10)	1.386(3)
C(10)-C(11)	1.385(4)	C(10)-C(11)	1.373(3)
C(11)-C(12)	1.379(4)	C(11)-C(12)	1.382(3)
C(11)-N(14)	1.461(3)	C(11)-N(14)	1.461(3)
C(12)-C(13)	1.380(4)	C(12)-C(13)	1.382(3)
N(14)-O(15)	1.215(4)		
N(14)-O(16)	1.234(4)		
o-ClPhTCA		p-ClPhTCA	
Cl(1)-C(4)	1.758(2)	Cl(1)-C(4)	1.764(4)
Cl(2)-C(4)	1.769(2)	Cl(2)-C(4)	1.767(4)
Cl(3)-C(4)	1.770(2)	Cl(3)-C(4)	1.743(4)
C(4)-C(5)	1.561(3)	C(4)-C(5)	1.555(5)
C(5)-O(6)	1.207(2)	C(5)-O(6)	1.210(4)
C(5)-N(7)	1.340(2)	C(5)-N(7)	1.328(4)
N(7)-C(8)	1.420(3)	N(7)-C(8)	1.416(4)
C(8)-C(9)	1.384(3)	C(8)-C(9)	1.381(5)
C(8)-C(13)	1.390(3)	C(8)-C(13)	1.387(5)
C(9)-C(10)	1.391(3)	C(9)-C(10)	1.378(5)
C(10)-C(11)	1.368(4)	C(10)-C(11)	1.374(5)
C(11)-C(12)	1.384(4)	C(11)-C(12)	1.368(5)
C(12)-C(13)	1.381(4)	C(12)-C(13)	1.380(5)
C(9)-Cl(14)	1.737(2)	C(11)-Cl(14)	1.740(4)

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

Connection	Bond angle	Connection	Bond angle
m-NO_2PhTCA			
C(5)-C(4)-Cl(1)	110.3(2)	C(21)-C(20)-Cl(17)	108.5(2)
C(5)-C(4)-Cl(2)	108.1(2)	C(21)-C(20)-Cl(18)	110.3(2)
C(5)-C(4)-Cl(3)	110.2(2)	C(21)-C(20)-Cl(19)	109.8(2)
Cl(1)-C(4)-Cl(2)	110.3(2)	Cl(17)-C(20)-Cl(18)	108.7(2)
Cl(1)-C(4)-Cl(3)	109.3(2)	Cl(17)-C(20)-Cl(19)	109.4(2)
Cl(2)-C(4)-Cl(3)	108.6(2)	Cl(18)-C(20)-Cl(19)	110.1(2)
O(6)-C(5)-N(7)	125.1(3)	O(22)-C(21)-N(23)	125.1(3)
O(6)-C(5)-C(4)	120.8(3)	O(22)-C(21)-C(20)	120.7(3)
N(7)-C(5)-C(4)	114.1(3)	N(23)-C(21)-C(20)	114.2(2)
C(5)-N(7)-C(8)	126.0(3)	C(21)-N(23)-C(24)	126.6(3)
C(9)-C(8)-C(13)	120.2(3)	C(25)-C(24)-C(29)	119.6(3)
C(9)-C(8)-N(7)	122.5(3)	C(25)-C(24)-N(23)	123.2(3)
C(13)-C(8)-N(7)	117.3(3)	C(29)-C(24)-N(23)	117.1(3)
C(10)-C(9)-C(8)	117.8(3)	C(24)-C(25)-C(26)	117.6(3)
C(9)-C(10)-C(11)	123.4(3)	C(27)-C(26)-C(25)	123.7(3)
C(9)-C(10)-N(14)	118.2(3)	C(27)-C(26)-N(30)	118.3(3)
C(11)-C(10)-N(14)	118.4(3)	C(25)-C(26)-N(30)	118.0(3)
C(12)-C(11)-C(10)	117.3(3)	C(26)-C(27)-C(28)	117.8(3)
C(13)-C(12)-C(11)	121.3(4)	C(27)-C(28)-C(29)	120.3(3)
C(12)-C(13)-C(8)	119.9(3)	C(28)-C(29)-C(24)	120.9(3)
O(15)-N(14)-O(16)	123.3(3)	O(31)-N(30)-O(32)	124.0(4)
O(15)-N(14)-C(10)	118.5(3)	O(31)-N(30)-C(26)	118.0(3)
O(16)-N(14)-C(10)	118.2(3)	O(32)-N(30)-C(26)	118.1(4)
p-NO_2PhTCA		PhTCA	
C(5)-C(4)-Cl(1)	109.1(2)	C(5)-C(4)-Cl(1)	113.4(1)
C(5)-C(4)-Cl(2)	108.3(2)	C(5)-C(4)-Cl(2)	110.0(1)
C(5)-C(4)-Cl(3)	111.7(2)	C(5)-C(4)-Cl(3)	106.9(1)
Cl(1)-C(4)-Cl(2)	108.7(2)	Cl(1)-C(4)-Cl(2)	108.4(1)
Cl(1)-C(4)-Cl(3)	109.7(2)	Cl(1)-C(4)-Cl(3)	109.5(1)
Cl(2)-C(4)-Cl(3)	109.4(2)	Cl(2)-C(4)-Cl(3)	108.6(1)
O(6)-C(5)-N(7)	126.5(2)	O(6)-C(5)-N(7)	126.3(2)
O(6)-C(5)-C(4)	119.7(2)	O(6)-C(5)-C(4)	118.9(1)
N(7)-C(5)-C(4)	113.7(2)	N(7)-C(5)-C(4)	114.8(1)
C(5)-N(7)-C(8)	126.6(2)	C(5)-N(7)-C(8)	125.4(1)
C(9)-C(8)-C(13)	120.0(2)	C(9)-C(8)-C(13)	119.9(2)
C(9)-C(8)-N(7)	117.6(2)	C(9)-C(8)-N(7)	122.1(2)
C(13)-C(8)-N(7)	122.4(2)	C(13)-C(8)-N(7)	117.9(2)
C(10)-C(9)-C(8)	120.6(2)	C(10)-C(9)-C(8)	119.5(2)
C(9)-C(10)-C(11)	118.5(2)	C(9)-C(10)-C(11)	120.7(2)
C(10)-C(11)-N(14)	119.1(3)	C(12)-C(11)-C(10)	119.7(2)
C(12)-C(11)-N(14)	118.6(3)	C(13)-C(12)-C(11)	120.4(2)
C(12)-C(11)-C(10)	122.3(2)	C(12)-C(13)-C(8)	119.8(2)
C(13)-C(12)-C(11)	119.0(2)		
C(12)-C(13)-C(8)	119.5(2)		
O(15)-N(14)-O(16)	123.1(3)		
O(15)-N(14)-C(11)	119.4(3)		
O(16)-N(14)-C(11)	117.5(3)		

compounds. We report now our results on the compounds, N-(3-nitrophenyl)-2,2,2-trichloroacetamide, 3-$NO_2C_6H_4$.NHCO.CCl_3 (**m-NO_2PhTCA**); N-(4-nitrophenyl)-2,2,2-trichloroacetamide, 4-$NO_2C_6H_4$.NHCO.CCl_3 (**p-NO_2PhTCA**); N-(2-chlorophenyl)-2,2,2-trichloroacetamide, 2-ClC_6H_4.NHCO.CCl_3 (**o-ClPhTCA**) and N-(4-chlorophenyl)-2,2,2-trichloroacetamide, 4-ClC_6H_4.NHCO.CCl_3 (**p-ClPhTCA**). Further, we have analaysed the present data along with our earlier crystal structures of N-(2-nitrophenyl)-2,2,2-trichloroacetamide, 2-$NO_2C_6H_4$.NHCO.CCl_3

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

Connection	Bond angle	Connection	Bond angle
o-ClPhTCA		p-ClPhTCA	
C(5)-C(4)-Cl(1)	110.7(1)	C(5)-C(4)-Cl(1)	109.5(3)
C(5)-C(4)-Cl(2)	108.9(1)	C(5)-C(4)-Cl(2)	108.6(3)
C(5)-C(4)-Cl(3)	109.4(1)	C(5)-C(4)-Cl(3)	110.9(2)
Cl(1)-C(4)-Cl(2)	109.0(1)	Cl(1)-C(4)-Cl(2)	109.3(2)
Cl(1)-C(4)-Cl(3)	108.3(1)	Cl(1)-C(4)-Cl(3)	108.9(2)
Cl(2)-C(4)-Cl(3)	110.5(1)	Cl(2)-C(4)-Cl(3)	109.7(2)
O(6)-C(5)-N(7)	125.8(2)	O(6)-C(5)-N(7)	126.0(3)
O(6)-C(5)-C(4)	120.1(2)	O(6)-C(5)-C(4)	119.6(3)
N(7)-C(5)-C(4)	114.1(2)	N(7)-C(5)-C(4)	114.4(3)
C(5)-N(7)-C(8)	122.4(2)	C(5)-N(7)-C(8)	125.6(3)
C(9)-C(8)-C(13)	119.0(2)	C(9)-C(8)-C(13)	119.6(3)
C(9)-C(8)-N(7)	119.9(2)	C(9)-C(8)-N(7)	122.2(3)
C(13)-C(8)-N(7)	121.1(2)	C(13)-C(8)-N(7)	118.2(3)
C(10)-C(9)-C(8)	120.9(2)	C(10)-C(9)-C(8)	119.8(3)
C(9)-C(10)-C(11)	119.5(2)	C(9)-C(10)-C(11)	119.8(3)
C(8)-C(9)-Cl(14)	120.2(2)	C(10)-C(11)-Cl(14)	119.1(3)
C(10)-C(9)-Cl(14)	118.9(2)	C(12)-C(11)-Cl(14)	119.6(3)
C(12)-C(11)-C(10)	120.3(2)	C(12)-C(11)-C(10)	121.3(3)
C(13)-C(12)-C(11)	120.4(2)	C(13)-C(12)-C(11)	119.0(3)
C(12)-C(13)-C(8)	119.9(2)	C(12)-C(13)-C(8)	120.5(3)

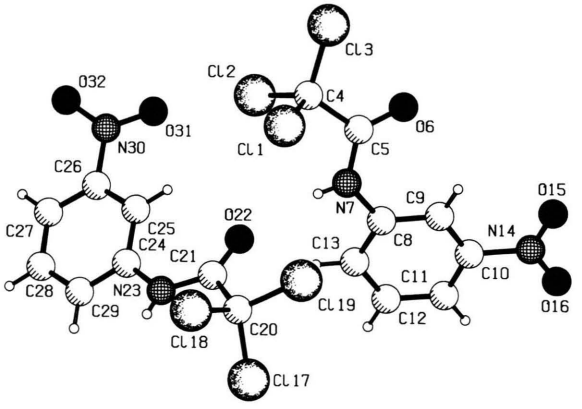

Fig. 1. Molecular geometry of N-(3-nitrophenyl)-2,2,2-trichloroacetamide, $3\text{-}NO_2C_6H_4.NHCO.CCl_3$ (**m-NO_2PhTCA**), with the numbering of atoms and thermal ellipsoids.

(**o-NO_2PhTCA**); N-(4-methylphenyl)-2,2,2-trichloroacetamide, $4\text{-}CH_3C_6H_4.NHCO.CCl_3$ (**p-CH_3PhTCA**) [19]; N-(phenyl)-2,2,2-trichloroacetamide, $C_6H_5.NHCO.CCl_3$ (**PhTCA**); N-chloro-N-(phenyl)-2,2,2-trichloroacetamide, $C_6H_5.NClCO.CCl_3$ (**NClPhTCA**) [8] and finally with N-(phenyl)acetamide, $C_6H_5.NHCO.CH_3$ (**PhA**) [20].

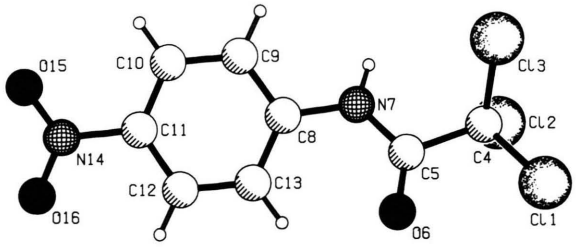

Fig. 2. Molecular geometry of N-(4-nitrophenyl)-2,2,2-trichloroacetamide, $4\text{-}NO_2C_6H_4.NHCO.CCl_3$ (**p-NO_2PhTCA**), with the numbering of atoms and thermal ellipsoids.

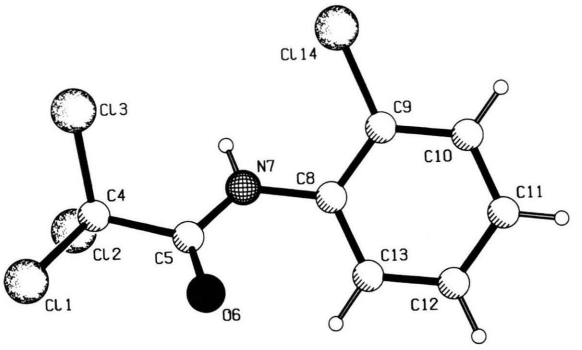

Fig. 3. Molecular geometry of N-(2-chlorophenyl)-2,2,2-trichloroacetamide, $2\text{-}ClC_6H_4.NHCO.CCl_3$ (**o-ClPhTCA**), with the numbering of atoms and thermal ellipsoids.

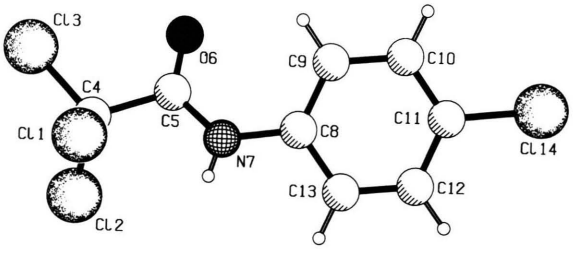

Fig. 4. Molecular geometry of N-(4-chlorophenyl)-2,2,2-trichloroacetamide, $4\text{-}ClC_6H_4.NHCO.CCl_3$ (**p-ClPhTCA**), with the numbering of atoms and thermal ellipsoids.

Experimental

Preparation and Characterisation of the Compounds

The compounds, **m-NO_2PhTCA**, **p-NO_2PhTCA**, **o-ClPhTCA**, and **p-ClPhTCA** were prepared from the corresponding mononitro or monochloroanilines, trichloroacetic acid and phosphoryl chloride (Aldrich, Germany) [4, 10, 21]. The commercial anilines were

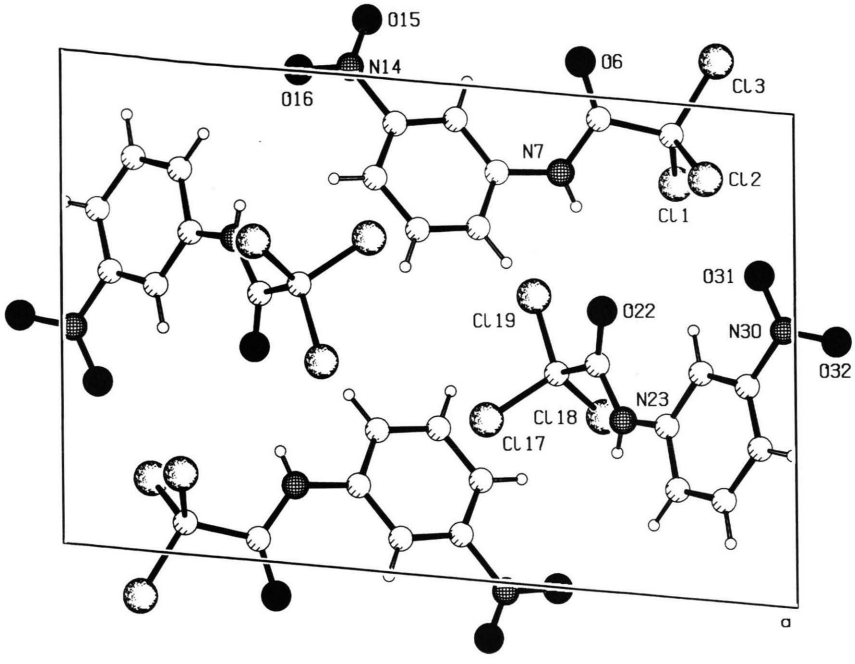

Fig. 5. Projection of the unit cell of **m-NO_2PhTCA** along the [100] *a* axis.

purified by zone refining. The liquids were purified by double distillation. The compounds were obtained by treating monosubstituted aniline with a clear mixture of trichloroacetic acid with phosphoryl chloride under constant stirring. The mixture was slowly warmed to expel HCl. Excess phosphoryl chloride was hydrolysed by adding cold 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 was checked by elemental analysis (C, H, and N) and by determining their melting points. The compounds **m-NO_2PhTCA**, **p-NO_2PhTCA**, **o-ClPhTCA**, and **p-ClPhTCA** were further characterised by recording their infrared and ^{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.

X-ray Diffraction Studies

Small fine crystals of **m-NO_2PhTCA**, **p-NO_2PhTCA**, **o-ClPhTCA** and **p-ClPhTCA** 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) [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. Further experimental conditions for structure determinations and refinements are given in Table 1.

Results and Discussion

The crystallographic data of the compounds, **m-NO_2PhTCA**, **p-NO_2PhTCA**, **o-ClPhTCA** and **p-ClPhTCA** are given in Table 1. The atomic coordinates and the mean displacement parameters are listed in Table 2, while Tables 3 and 4 give the intramolecular bond distances and bond angles, respectively. The latter tables also contain the bond distances and bond angles for the parent compound **PhTCA**. The hydrogen coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations will be deposited at the Cambridge Crystallographic Data Centre, CDCS numbers 147590 - 147593. Figures 1 - 4 show the molecules of the title compounds, **m-NO_2PhTCA**, **p-NO_2PhTCA**, **o-ClPhTCA** and **p-ClPhTCA** as they appear in suitable projection with their thermal ellipsoids and with the numbering of the atoms used throughout the paper. The projections of the unit cells of the compounds,

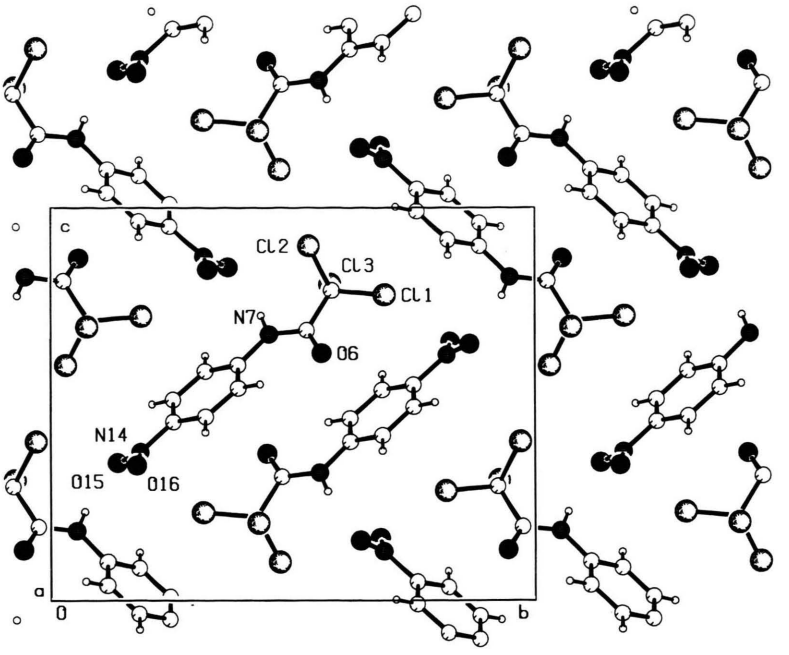

Fig. 6. Projection of the unit cell of **p-NO_2PhTCA** along the [100] *a* axis.

m-NO_2PhTCA, **p-NO_2PhTCA**, **o-ClPhTCA** and **p-ClPhTCA** are shown in Figures 4 - 8.

The compounds, **m-NO_2PhTCA**, **o-NO_2PhTCA**, and **p-CH_3PhTCA** show two molecules each in their asymmetric units. This is in agreement with the multiple lines observed in the ^{35}Cl NQR spectra of the compounds **o-NO_2PhTCA** and **p-CH_3PhTCA** [10]. But the compound **m-NO_2PhTCA** showed only 3 ^{35}Cl NQR frequencies at 77 K, and these ^{35}Cl(ω) NQR frequencies fade out at room temperature. Hence the presence of two molecules in the asymmetric unit indicates that this compound may undergo a phase transition below room temperature.

The phenyl, N-chloro-phenyl, 4-nitrophenyl and 4-methylphenyl trichloroacetamides crystallise in the monoclinic crystal symmetry, while the 2-nitrophenyl and 3-nitrophenyl trichloroacetamides crystallise in the triclinic crystal system, whereas 2-chlorophenyl and 4-chlorophenyl trichloroacetamides and N-phenyl acetamide crystallise with orthorhombic symmetry. It may be difficult to generalise these aspects, unless an extensive work is carried out with the change of both the substituent and the site of substitution in the phenyl ring. Work is in progress in our group in this direction.

If we now turn to the intramolecular geometry of the four title compounds, **m-NO_2PhTCA**, **p-NO_2PhTCA**, **o-ClPhTCA**, and **p-ClPhTCA**, in comparison with the compounds **o-NO_2PhTCA, p-CH_3PhTCA, PhTCA, NClPhTCA**, and **PhA**, we find that the range of C(i)-C(j) bond distances within the phenyl rings of the compounds shows no significant changes with the substitution either at the side chain or in the phenyl ring. The mean distances of all the compounds lie in the range 1.377 - 1.387 Å, the minimum mean value has N-chloro-N-phenyl trichloroacetamide (**NClPhTCA**) and the maximum mean value N-phenyl acetamide (**PhA**). Also the range of the six ring distances for the compound **PhA** is wider (1.366 - 1.413 Å), which narrows down on substitution either in the phenyl ring or at the side chain, the narrowest range being 1.373 - 1.390 Å for the **PhTCA**, with most of the ring distances of all the compounds being in the range of 1.37 - 1.39 Å. The C(ring)-Cl distances for the compounds **o-ClPhTCA** and **p-ClPhTCA** are 1.737 and 1.740 Å. The C(ring) - N distances for the compounds, **o-NO_2PhTCA**, **m-NO_2PhTCA**, **p-NO_2PhTCA**, **o-ClPhTCA**, **p-ClPhTCA**, **p-CH_3PhTCA**, **PhTCA**, **NClPhTCA**, and **PhA** are 1.402, 1.414, 1.415, 1.420, 1.416, 1.427, 1.424, 1.443 and 1.426 Å, respectively. The minimum and maximum distances of 1.402 Å and 1.443 Å are for the 2-nitrophenyl and N-chloro phenyl trichloroacetamides, respectively. Only N-chlorination or the substitution of a strong electron withdrawing group at the ortho position of the phenyl

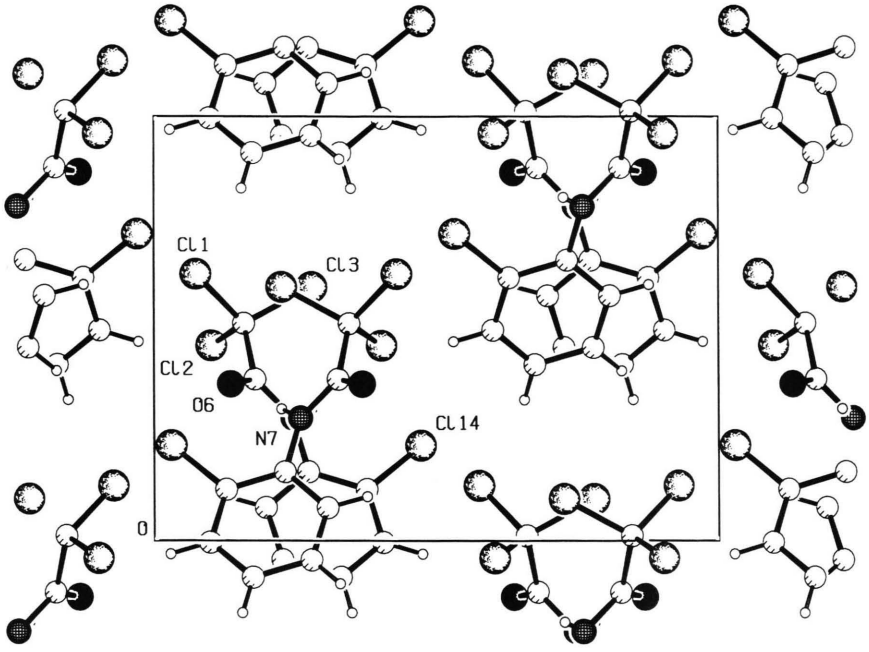

Fig. 7. Projection of the unit cell of **o-ClPhTCA** along [100] on to the *bc* plane.

ring affects the C(ring)-N distance in this class of compounds. There is no significant change in the C(O)-N bond distance on substitution, the trend being more or less as that for the C(ring)-N distance, while the C-O bond length is slightly shortened with the replacement of the $-CH_3$ group by $-CCl_3$, by the introduction of electron withdrawal groups into the phenyl ring or N-chlorination of the amide. Thus it is 1.226 Å for the N-phenyl acetamide (**PhA**), 1.195 Å for the 2-nitro or 4-nitrophenyl trichloroacetamide and 1.200 Å for the N-chloro-N-chloro trichloroacetamide. The C(O)-C(side) bond lengths remain in the range of 1.555 - 1.565 Å for all the compounds, except for the phenyl acetamide, for which it is 1.476 Å. This distance increases to the above range on substitution in the side chain. The mean C(side)-Cl bond length generally remains in the range of 1.760 - 1.765 Å.

As regards the bond angles, they are observed between the ranges listed as follows: 116.9° and 121.6° (**o-NO_2TCA**), 117.3° and 123.7° (**m-NO_2PhTCA**), 118.5° and 122.3° (**p-NO_2PhTCA**), 119.0°, and 120.9° (**o-ClPhTCA**), 119.0° and 121.3° (**p-ClPhTCA**), 116.8° and 122.4°, (**p-CH_3PhTCA**), 119.5° and 120.7° (**PhTCA**), 118.6° and 121.5° (**NClPhTCA**), and 119.2° and 121.3° (**PhA**) with the mean values of 120° in all the cases. The deviations of the individual values from 120° are relatively larger for the nitro and methyl substituted trichloroacetamides. The C2(ring)-C1(ring)-N and C6(ring)-C1(ring)-N angles for all the nine compounds are 121.2° and 121.8° (**o-NO_2PhTCA**), 122.9° and 117.2° (**m-NO_2PhTCA**), 117.6° and 122.4° (**p-NO_2PhTCA**), 119.9° and 121.1° (**o-ClPhTCA**), 122.2° and 118.1° (**p-ClPhTCA**), 119.4° and 121.2° (**p-CH_3PhTCA**), 122.1° and 117.9° (**PhTCA**), 119.6° and 118.8° (**NClPhTCA**) and 115.7° and 122.7° (**PhA**). Similarly the C2(ring)-C1(ring)-C6(ring) bond angles are 117.0°, 119.9°, 120.0°, 119.0°, 119.6° , 119.3°, 119.9°, 121.5° and 121.2° for the compounds, **o-NO_2PhTCA**, **m-NO_2PhTCA**, **p-NO_2PhTCA**, **o-ClPhTCA**, **p-ClPhTCA**, **p-CH_3PhTCA**, **PhTCA**, **NClPhTCA** and **PhA**, respectively. Within these compounds the C(ring)-N-C(O) bond angles vary as 127.9° (**o-NO_2TCA**), 126.3° (**m-NO_2PhTCA**), 126.6° (**p-NO_2PhTCA**), 122.4° (**o-ClPhTCA**), 125.6° (**p-ClPhTCA**), 124.1° (**p-CH_3PhTCA**), 125.4° (**PhTCA**), 132.3° (**NClPhTCA**) and 129.3° (**PhA**), while the N-C(O)-C(side chain) angles are 113.7° (**o-NO_2TCA**), 114.2° (**m-NO_2PhTCA**), 113.7° (**p-NO_2PhTCA**), 114.1° (**o-ClPhTCA**), 114.4° (**p-ClPhTCA**), 116.5° (**p-CH_3PhTCA**), 114.8° (**PhTCA**), 118.6° (**NClPhTCA**) and 117.7° (**PhA**), respectively. Similarly the O-C(O)-C(side chain) angles vary as 118.9° (**o-NO_2PhTCA**), 120.8° (**m-NO_2PhTCA**), 119.7° (**p-NO_2PhTCA**),

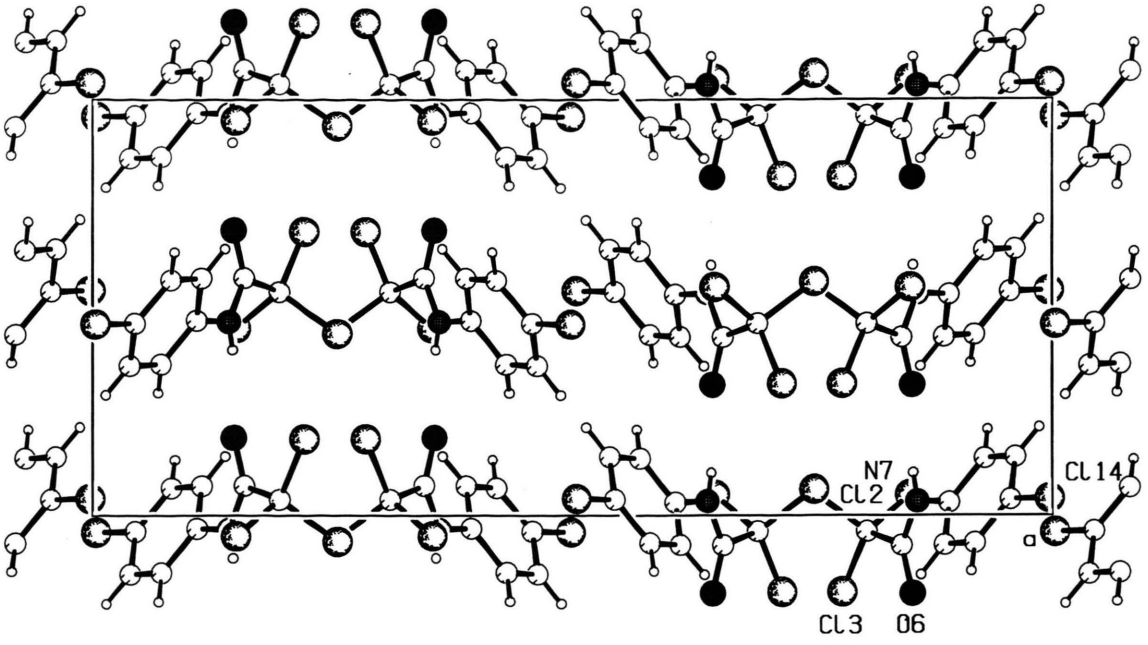

Fig. 8. Projection of the unit cell of **p-ClPhTCA** along [100] on to the *bc* plane.

120.1° (**o-ClPhTCA**), 119.6° (**p-ClPhTCA**), 118.2° (**p-CH_3PhTCA**), 118.9° (**PhTCA**), 118.3° (**NClPhTCA**) and 120.4° (**PhA**), while the O-C(O)-N angles for the compounds are 127.4° (**o-NO_2TCA**), 125.1° (**m-NO_2PhTCA**), 126.5° (**p-NO_2PhTCA**), 125.8° (**o-ClPhTCA**), 126.0° (**p-ClPhTCA**), 125.3° (**p-CH_3PhTCA**), 126.3° (**PhTCA**), 123.0° (**NClPhTCA**) and 121.7° (**PhA**).

Acknowledgements

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[1] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, Nuclear Quadrupole Resonance in Chemistry; Wiley & Sons, New York 1975.

[2] J. A. S. Smith (Ed.), Advances in Nuclear Quadrupole Resonances; Wiley & Sons, London 1974-83. Vols. **1 - 5**.

[3] D. Biedenkapp and Al. Weiss, J. Chem. Phys. **49**, 3933 (1968).

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

[5] Al. Weiss and S. Wigand, Z. Naturforsch. **45a,** 195 (1990).

[6] Al. Weiss, Z. Naturforsch. **48a,** 477 (1993); Acta Cryst. **B51,** 523 (1995).

[7] B. T. Gowda and Al. Weiss, Z. Naturforsch. **49a,** 695 (1994).

[8] S. Dou, B. T. Gowda, H. Paulus, and Al. Weiss, Z. Naturforsch. **49a,** 1136 (1994).

[9] B. T. Gowda, S. Dou, and Al. Weiss, Z. Naturforsch. **51a,** 627 (1996).

[10] B. T. Gowda, D. K. Bhat, H. Fuess, and Al. Weiss, Z. Naturforsch. **54a**, 261 (1999).

[11] B. T. Gowda, D. K. Bhat, H. Fuess, and Al. Weiss, Z. Naturforsch., **54a**, 679 (1999).

[12] B. T. Gowda, B. H. A. Kumar, and H. Fuess, Z. Naturforsch. Submitted for publication.

[13] The Chemistry of Amides, ed. J. Jabicky; Interscience, London 1970.

[14] R. Sandler and W. Karo, Organic Functional Group Preparations; Academic Press, London 1972, Vol. **3**.

[15] K. Hargreaves, J. G. Pritchard, and H. R. Dave, Chem. Rev. **70,** 439 (1970).

[16] E. Stewart and T. H. Siddal, Chem. Rev. **70,** 517 (1970).
[17] S. Isaacs, Chem. Soc. Rev. **5,** 181 (1976).
[18] D. K. Bhat and B. T. Gowda, J. Indian Chem. Soc. **77,** 279 (2000).
[19] S. Dou, H. Fuess, Al. Weiss, B. T. Gowda, and V. G. Krishnan, Z. Kristallogr. **212,** 532 (1997).
[20] a) C. J. Brown and D. E. C. Corbridge, Acta Cryst. **7,** 711 (1954); b) C. J. Brown, Acta Cryst. **21,** 442 (1966).
[21] F. A. Berti and L. M. Ziti, Arch. Pharm. **285,** 372 (1952).
[22] M. Sheldrick: SHELXS-86. Program for the Solution of Crystal Structures, University of Göttingen, Germany 1986
[23] M. Sheldrick: SHELXL-93. Program for Crystal Structure Determination, University of Göttingen, Germany 1993
[24] Nonius Diffractometer Control Software (1993), NONIUS GmbH, Solingen, Germany 1993.
[25] L. Spek: PLUTON-93. Program for the Display and Analysis of Crystal and Molecular Structures, University of Utrecht, The Netherlands 1993.
[26] C. T. North, D. C. Philips and F. S. Mathews, Acta Cryst. **A24,** 351 (1968).
[27] D. Flack, Acta Cryst. **A39,** 876 (1983).