Structural Studies on *N*-(Phenyl)-2,2,2-trimethyl-acetamide, *N*-(2,4,6-Trimethylphenyl)-2,2,2-trimethyl-acetamide and *N*-(2,4,6-Trimethylphenyl)-2,2,2-trichloro-acetamide, 2,4,6-$X_3C_6H_2NH$-CO-CY_3 (X = H or CH_3; Y = CH_3 or Cl)

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To study the effect of side chain and ring substitutions on the solid state geometry of amides of the general formulae C_6H_5NH-CO-CX_3 and 2,4,6-$X_3C_6H_2NH$-CO-$CH_{3-y}X_y$ (X = CH_3 or Cl and $y = 0, 1, 2, 3$), crystal structures of *N*-(phenyl)-2,2,2-trimethyl-acetamide, C_6H_5NH-CO-$C(CH_3)_3$ (**PTMA**); *N*-(2,4,6-trimethylphenyl)-2,2,2-trimethyl-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$C(CH_3)_3$ (**TMPTMA**) and *N*-(2,4,6-trimethylphenyl)-2,2,2-trichloro-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CCl_3 (**TMPTCA**) have been determined. The data are analyzed along with those of *N*-(phenyl)-acetamide, C_6H_5NH-CO-CH_3; *N*-(phenyl)-2,2,2-trichloro-acetamide, C_6H_5NH-CO-CCl_3; *N*-(2,4,6-trimethylphenyl)-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3; *N*-(2,4,6-trimethylphenyl)-2-chloro-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2Cl; *N*-(2,4,6-trimethylphenyl)-2,2-dichloro-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$; *N*-(2,4,6-trimethylphenyl)-2-methyl-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3; *N*-(2,4,6-trimethylphenyl)-2,2-dimethyl-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH(CH_3)_2$; *N*-(2,4,6-trichlorophenyl)-acetamide, 2,4,6-$Cl_3C_6H_2$-NH-CO-CH_3; *N*-(2,4,6-trichlorophenyl)-2-chloro-acetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-CH_2Cl; *N*-(2,4,6-trichlorophenyl)-2,2-dichloro-acetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-$CHCl_2$ and *N*-(2,4,6-trichlorophenyl)-2,2,2-trichloro-acetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-CCl_3. The crystallographic system, space group, formula units and lattice constants in Å are: **PTMA**: orthorhombic, $Pca2_1$, $Z = 4$, $a = 9.969(3)$, $b = 10.642(3)$, $c = 10.172(3)$; **TMPTMA**: tetragonal, $P4_12_12$, $Z = 8$, $a = 12.708(3)$, $b = 12.708(3)$, $c = 17.354(4)$; **TMPTCA**: monoclinic, $P2_1/n$, $Z = 8$, $a = 12.255(4)$, $b = 17.904(6)$, $c = 12.619(4)$, $\beta = 95.23(2)^\circ$. **PTMA** and **TMPTMA** have 1 molecule each in their asymmetric units, but **TMPTMA** shows disorder. **TMPTCA** has 2 molecules in its asymmetric unit. The comparison of the bond parameters reveals that there are significant changes in the structural parameters with ring and side chain substitutions.

Key words: Crystal Structures; *N*-(Phenyl)-2,2,2-trimethyl-acetamide; *N*-(2,4,6-Trimethylphenyl)-2,2,2-trimethyl-/trichloro-acetamides.

1. Introduction

The knowledge of the structure of materials is essential for a proper understanding of their physical and chemical properties. Thus crystal structure studies have been extensively used to investigate the structural aspects of a variety of compounds. Amides are of fundamental chemical interest as conjugation between nitrogen lone pair electrons and the carbonyl π-bond results in distinct physical and chemical properties. The amide moiety is an important constituent of many biologically significant compounds. 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, fungicidal and herbicidal activities. This has further stimulated interest in their chemistry.

To study the effect of side chain and benzene ring substitutions on the -NHCO- bond parameters in substituted amides, we have studied the crystal structures of several amides [1 – 6]. As part of continuing studies in this direction, we report herein the structural studies on *N*-(phenyl)-2,2,2-trimethyl-acetamide, C_6H_5NH-CO-$C(CH_3)_3$ (**PTMA**); *N*-(2,4,6-trimethylphenyl)-2,2,2-trimethyl-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of *N*-(phenyl)-2,2,2-trimethyl-acetamide, $C_6H_5NH\text{-}CO\text{-}C(CH_3)_3$ (**PTMA**); *N*-(2,4,6-trimethylphenyl)-2,2,2-trimethyl-acetamide, 2,4,6-$(CH_3)_3$-$C_6H_2NH\text{-}CO\text{-}C(CH_3)_3$ (**TMPTMA**) and *N*-(2,4,6-trimethylphenyl)-2,2,2-trichloro-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO\text{-}CCl_3$ (**TMPTCA**). Diffractometer: Stoe-Stadi4; monochromator: graphite (002); scan $2\theta/\omega = 1/1$; refinement method: full-matrix least-squares on F^2.

Description	**PTMA**	**TMPTMA**	**TMPTCA**
Chemical formula	$C_{11}H_{15}NO$	$C_{14}H_{21}NO$	$C_{11}H_{12}C_{l3}NO$
Formula mass, g mol^{-1}	177.24	219.32	280.57
Temperature, K	298(2)	299(2)	300(2)
Wavelength, pm	71.069	71.069	71.069
Crystal system	orthorhombic	tetragonal	monoclinic
Space group	$Pca2_1$	$P4_12_12$	$P2_1/n$
a, Å	9.969(3)	12.708(3)	12.255(4)
b, Å	10.642(3)	12.708(3)	17.904(6)
c, Å	10.172(3)	17.354(4)	12.619(4)
β, deg.	90	90	95.23(2)
Volume, Å^3	1079.1(5)	2802.6(11)	2757.3(16)
Z	4	8	8
Density (calculated), g cm^{-3}	1.091	1.040	1.352
Absorption coefficient, cm^{-1}	0.70	0.65	6.44
$F(000)$	384	960	1152
Crystal size, mm^3	$4.50 \times 0.20 \times 0.15$	$6.00 \times 0.20 \times 0.20$	$3.50 \times 0.30 \times 0.15$
θ Range, deg.	1.91 to 22.47	1.99 to 22.47	1.98 to 24.99
Index ranges	$0 \le h \le 10$, $-11 \le k \le 2$, $-10 \le l \le 10$	$0 \le h \le 13$, $0 \le k \le 13$, $-18 \le l \le 2$	$-14 \le h \le 14$, $-21 \le k \le 3$, $0 \le l \le 14$
Reflections collected	1664	2257	5830
Independent reflections	1408	1829	4832
R(int)	0.0139	0.0121	0.0108
Completeness to θ	22.47 100.0%	22.47 100.0%	24.99 99.9%
Absorption correction	none	none	numerical
Max. and min. transmission	0.9896 and 0.7445	0.9872 and 0.6980	0.914 and 0.813
Data	1408	1829	4832
Restraints/parameters	1/125	0/172	0/301
Goodness-of-fit on F^2	1.123	1.095	1.039
Final R $[I > 2\sigma(I)]$	$R1 = 0.0368$, $wR2 = 0.0902$	$R1 = 0.0430$, $wR2 = 0.1070$	$R1 = 0.0867$, $wR2 = 0.2427$
R Indices (all data)	$R1 = 0.0387$, $wR2 = 0.0924$	$R1 = 0.0579$, $wR2 = 0.1178$	$R1 = 0.1204$, $wR2 = 0.2831$
Absolute structure parameter	0.6(19)	$-2(3)$	–
Extinction coefficient	0.211(12)	0.0060(10)	–
Largest diff. peak and hole, e Å^{-3}	0.148 and -0.110	0.107 and -0.109	0.919 and -0.611

$CH(CH_3)_3$ (**TMPTMA**) and *N*-(2,4,6-trimethylphenyl)-2,2,2-trichloro-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO\text{-}CHCl_3$ (**TMPTCA**). The structural data have been compared with those of *N*-(phenyl)-acetamide, $C_6H_5NH\text{-}CO\text{-}CH_3$ (**PA**) [7]; *N*-(phenyl)-2,2,2-trichloro-acetamide, $C_6H_5NH\text{-}CO\text{-}CCl_3$ (**PTCA**) [8]; *N*-(2,4,6-trimethylphenyl)-acetamide, 2,4,6-$(CH_3)_3$-$C_6H_2NH\text{-}CO\text{-}CH_3$ (**TMPA**) [6]; *N*-(2,4,6-trimethylphenyl)-2-chloro-acetamide, 2,4,6-$(CH_3)_3C_6H_2$-$NH\text{-}CO\text{-}CH_2Cl$ (**TMPCA**) [3]; *N*-(2,4,6-trimethylphenyl)-2,2-dichloro-acetamide, 2,4,6-$(CH_3)_3C_6H_2$-$NH\text{-}CO\text{-}CHCl_2$ (**TMPDCA**); *N*-(2,4,6-trimethylphenyl)-2-methyl-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO$-$CH_2CH_3$ (**TMPMA**); *N*-(2,4,6-trimethylphenyl)-2,2-dimethyl-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO$-$CH(CH_3)_2$ (**TMPDMA**) [6]; *N*-(2,4,6-trichlorophenyl)-acetamide, 2,4,6-$Cl_3C_6H_2NH\text{-}CO\text{-}CH_3$ (**TCPA**) [9]; *N*-(2,4,6-trichlorophenyl)-2-chloro-acetamide, 2,4,6-$Cl_3C_6H_2NH\text{-}CO\text{-}CH_2Cl$ (**TCPCA**); *N*-(2,4,6-trichlorophenyl)-2,2-dichloro-acetamide, 2,4,6-$Cl_3C_6H_2NH\text{-}CO\text{-}CHCl_2$ (**TCPDCA**) and *N*-(2,4,6-trichlorophenyl)-2,2,2-trichloro-acetamide, 2,4,6-$Cl_3C_6H_2NH\text{-}CO\text{-}CCl_3$ (**TCPTCA**) [3]. The objective is to analyze the effect of substitutions in the side chain and in the benzene ring on the solid state structural geometry of amides of the following general configuration, $C_6H_5NH\text{-}CO\text{-}CX_3$ (X = CH_3 or Cl), 2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO\text{-}CH_{3-y}X_y$ (X = CH_3 or Cl; $y = 0, 1, 2, 3$) and 2,4,6-$Cl_3C_6H_2NH\text{-}CO\text{-}CH_{3-y}Cl_y$ ($y = 0, 1, 2, 3$).

Table 2. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters ($Å^2 \cdot 10^3$) of $C_6H_5NH\text{-}CO\text{-}C(CH_3)_3$; 2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO\text{-}C(CH_3)_3$ and 2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO\text{-}CCl_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
$C_6H_5NH\text{-}CO\text{-}C(CH_3)_3$				
C(1)	1083(2)	1310(2)	1854(2)	68(1)
C(2)	440(2)	795(3)	617(2)	99(1)
C(3)	124(2)	2209(3)	2539(4)	107(1)
C(4)	1431(3)	211(2)	2776(3)	99(1)
C(5)	2359(2)	2032(2)	1489(2)	58(1)
O(6)	2637(2)	2282(1)	351(1)	79(1)
N(7)	3145(2)	2389(1)	2501(2)	60(1)
C(8)	4371(2)	3065(2)	2421(2)	57(1)
C(9)	5224(2)	2961(2)	1359(2)	77(1)
C(10)	6424(2)	3606(3)	1355(3)	104(1)
C(11)	6785(3)	4342(3)	2391(5)	115(1)
C(12)	5946(3)	4436(2)	3460(3)	101(1)
C(13)	4734(2)	3802(2)	3483(3)	75(1)
2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO\text{-}C(CH_3)_3$				
C(1)	−2709(5)	3905(10)	211(4)	213(6)
C(2)	−2772(4)	5597(6)	866(7)	185(5)
C(3)	−3148(4)	3963(6)	1589(3)	143(3)
C(1′)	−2854(13)	4953(15)	297(10)	106(5)
C(2′)	−3116(10)	5120(11)	1668(7)	93(4)
C(3′)	−3030(11)	3356(11)	1027(10)	102(5)
C(4)	−2525(2)	4457(3)	986(2)	82(1)
C(5)	−1355(2)	4362(2)	1176(1)	65(1)
O(6)	−1059(2)	4008(2)	1796(1)	84(1)
N(7)	−668(2)	4661(2)	635(1)	66(1)
C(8)	447(2)	4620(2)	743(1)	62(1)
C(9)	989(2)	5544(2)	907(2)	71(1)
C(10)	2069(2)	5495(2)	980(2)	81(1)
C(11)	2615(2)	4566(3)	930(2)	81(1)
C(12)	2054(2)	3663(3)	783(2)	80(1)
C(13)	970(2)	3660(2)	684(1)	68(1)
C(14)	411(3)	6575(2)	1016(2)	102(1)
C(15)	3792(2)	4537(3)	1060(2)	113(1)
C(16)	377(3)	2658(2)	531(2)	92(1)

Atom	x	y	z	U(eq)
2,4,6-$(CH_3)_3C_6H_2NH\text{-}CO\text{-}CCl_3$				
Cl(1)	−953(2)	710(2)	1673(2)	144(1)
Cl(2)	−1215(1)	−593(1)	2934(3)	154(1)
Cl(3)	−598(2)	787(1)	3901(2)	139(1)
C(4)	−443(4)	206(3)	2820(5)	79(2)
C(5)	781(4)	9(3)	2736(4)	66(1)
O(6)	1070(3)	−633(2)	2784(4)	94(1)
N(7)	1429(3)	590(2)	2634(4)	69(1)
C(8)	2576(4)	522(2)	2494(5)	68(1)
C(9)	2909(5)	631(3)	1490(5)	78(1)
C(10)	4025(5)	588(3)	1372(6)	89(2)
C(11)	4781(5)	436(3)	2215(7)	94(2)
C(12)	4410(4)	332(3)	3191(6)	91(2)
C(13)	3308(4)	369(3)	3378(4)	74(1)
C(14)	2105(6)	801(4)	548(5)	97(2)
C(15)	5997(6)	380(5)	2066(8)	142(3)
C(16)	2931(5)	244(4)	4456(5)	97(2)
Cl(17)	1318(3)	3719(1)	4131(2)	183(1)
Cl(18)	1829(2)	2235(1)	4783(2)	142(1)
Cl(19)	3532(2)	3212(2)	4293(2)	169(1)
C(20)	2145(6)	2948(3)	3942(5)	94(2)
C(21)	1949(4)	2707(3)	2773(4)	71(1)
O(22)	1379(3)	2168(2)	2539(3)	91(1)
N(23)	2410(3)	3141(2)	2085(4)	71(1)
C(24)	2410(4)	2948(3)	977(4)	70(1)
C(25)	1451(5)	3038(3)	301(5)	87(2)
C(26)	1502(7)	2867(4)	−748(6)	109(2)
C(27)	2447(7)	2607(4)	−1141(5)	104(2)
C(28)	3376(6)	2519(3)	−437(5)	97(2)
C(29)	3382(5)	2687(3)	632(5)	79(1)
C(30)	413(5)	3312(4)	694(7)	120(2)
C(31)	2500(10)	2430(6)	−2325(6)	157(4)
C(32)	4371(5)	2578(4)	1386(5)	94(2)

2. Experimental

2.1. Preparation and Characterization of the Compounds

The compounds **PTMA**, **TMPTMA** and **TMPTCA** were prepared from the reaction of aniline or 2,4,6-trimethylaniline with (i) trimethyl- or trichloroacetylchlorides or (ii) trimethyl- or trichloroacetic acids (Aldrich, Germany) and phosphoryl chloride or thionyl chloride [10, 11]. The commercial aniline and 2,4,6-trimethylaniline were purified by double distillation. All other reagents employed in the preparations and purification of the compounds were of analytical grade. The compounds **PTMA** and **TMPTMA** were prepared by treating aniline and 2,4,6-trimethylaniline with trimethylacetyl chloride in acetone or benzene, while **TMPTCA** was prepared by treating 2,4,6-trimethylaniline with a clear mixture of 2,2,2-trichloroacetic acid with phosphoryl chloride/thionyl chloride under constant stirring. The resulting mixtures were slowly warmed to expel HCl. Excess phosphoryl chloride/thionyl chloride was hydrolyzed by adding cold water dropwise under ice-cold conditions. Produced HCl was removed by treating the reaction mixtures with 2 M NaOH. The separated solids were filtered under suction, washed thoroughly with water and dried. The compounds were recrystallized from ethanol several times. The purity of the compounds **PTMA**, **TMPTMA** and **TMPTCA** was checked by determining their melting points. The melting points (in °C) are: **PTMA**, 134; **TMPTMA**, 184; **TMPTCA**, 118. The compounds were further characterized by recording their infrared spectra and

Table 3. Comparison of crystal structure data of C_6H_5NH-CO-$C(CH_3)_3$ (**PTMA**); 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$C(CH_3)_3$ (**TMPTMA**) and 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CCl_3 (**TMPTCA**) with those of C_6H_5NH-CO-CH_3 (**PA**) [7]; C_6H_5NH-CO-CCl_3 (**PTCA**) [8]; 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3 (**TMPA**); 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3 (**TMPMA**); 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH(CH_3)_2$ (**TMPDMA**) [6]; 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2Cl (**TMPCA**) [3]; 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$ (**TMPDCA**) [6]; 2,4,6-$Cl_3C_6H_2NH$-CO-CH_3 (**TCPA**) [9]; 2,4,6-$Cl_3C_6H_2NH$-CO-CH_2Cl (**TCPCA**); 2,4,6-$Cl_3C_6H_2NH$-CO-$CHCl_2$ (**TCPDCA**) and 2,4,6-$Cl_3C_6H_2NH$-CO-CCl_3 (**TCPTCA**) [3].

Parameter	**PA**	**PTMA**	**PTCA**	**TMPA**	**TMPMA**	**TMPDMA**	**TMPTMA**	**TMPCA**	**TMPDCA**	**TMPTCA**	**TCPA**	**TCPCA**	**TCPDCA**	**TCPTCA**
Crystal system	ortho-rhombic	ortho-rhombic	mono-clinic	mono-clinic	mono-clinic	mono-clinic	tetra-gonal	mono-clinic	tri-clinic	mono-clinic	mono-clinic	ortho-rhombic	ortho-rhombic	tri-clinic
Space group	*Pbca*	*Pca*2$_1$	*P*21*c*	*Pn*	*P*21/*n*	*P*2$_1$/*c*	*P*4$_1$2$_1$2	*P*2$_1$/*n*	*P*1	*P*2$_1$/*n*	*Pn*	*Pna*2$_1$	*P*2$_1$2$_1$2	*P*1
Z	8	4	4	2	8	4	8	8	2	8	2	8	4	4
Bond lengths														
C(ring)-C(ring), mean	1.387	1.377	1.383	1.389	1.382	1.386	1.383	1.386	1.387	1.383	1.384	1.381	1.378	1.375
min.	1.366	1.362	1.373	1.382	1.371	1.372	1.371	1.359	1.368	1.364	1.374	1.361	1.355	1.350
max.	1.413	1.384	1.390	1.400	1.396	1.391	1.393	1.401	1.406	1.396	1.398	1.399	1.390	1.401
C(ring)-N	1.426	1.420	1.424	1.427	1.424	1.429	1.430	1.427	1.437	1.439	1.413	1.410	1.417	1.432
N-C(O)	1.330	1.348	1.337	1.337	1.330	1.343	1.337	1.320	1.330	1.325	1.357	1.345	1.316	1.332
C-O	1.226	1.219	1.211	1.225	1.224	1.224	1.225	1.231	1.199	1.208	1.221	1.216	1.235	1.193
C(O)-C(side)	1.476	1.532	1.564	1.495	1.498	1.513	1.528	1.510	1.532	1.545	1.499	1.513	1.511	1.531
Bond angles														
C(2r)-C(1r)-C(6r)	121.2	119.7	119.9	120.7	121.2	121.1	121.2	121.5	122.0	122.9	117.3	116.5	117.4	118.1
C(2r)-C(1r)-N	115.7	122.4	122.1	118.6	119.5	118.8	119.2	118.9	117.7	119.0	120.1	121.7	121.1	119.5
C(6r)-C(1r)-N	122.7	117.9	117.9	120.8	119.3	120.1	119.6	119.7	120.2	118.2	122.5	121.9	121.4	122.4
C(1r)-N-C(O)	129.3	126.8	125.4	124.6	124.7	123.1	123.0	123.9	122.4	122.7	123.2	123.0	124.4	119.9
N-C(O)-C(side)	117.7	116.1	114.8	115.4	115.8	116.5	117.5	114.7	113.1	115.0	114.8	113.9	115.4	116.0
N-C(O)-O	121.7	122.1	126.3	123.4	122.5	122.2	121.4	124.0	125.4	125.4	123.2	123.5	124.4	124.9
O-C(O)-C(side)	120.4	121.9	118.9	121.2	121.8	121.3	121.1	121.3	121.4	119.6	122.0	122.7	120.1	119.3

Fig. 1. Molecular geometry of *N*-(phenyl)-2,2,2-trimethyl-acetamide, C_6H_5NH-CO-$C(CH_3)_3$ (**PTMA**), with the numbering of atoms.

comparing the frequencies with the literature values [11].

2.2. Crystal Structure Studies

Small crystals of **PTMA**, **TMPTMA** and **TMPTCA** 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-97) [12 – 20]. 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 compounds **PTMA**, **TMPTMA** and **TMPTCA** are given 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 amides are compared in Table 3. In Table 4 we compare the available torsional angles for this category of compounds. The hydrogen coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations of **PTMA**, **TMPTMA** and **TMPTCA** have been deposited at the Cambridge Crystallographic Data Centre [CCDC, 12 Union Road, Cambridge, CB2IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk)]. The CCDC numbers are 239624, 239625 and 239626, respectively, for *N*-(phenyl)-2,2,2-trimethyl-acetamide, *N*-(2,4,6-trimeth-

Table 4. Comparison of significant torsional angles (degree) (standard deviations) of 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CCl_3 (**TMPTCA**) with those of 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3 (**TMPA**) [6]; 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3 (**TMPMA**); 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$ (**TMPDCA**); 2,4,6-$Cl_3C_6H_2NH$-CO-$CHCl_2$ (**TCPDCA**) and 2,4,6-$Cl_3C_6H_2NH$-CO-CCl_3 (**TCPTCA**) [3].

Connection	Torsional angle								
	TMPA	**TMPMA**		**TMPDCA**	**TCPDCA**	**TMPTCA**		**TCPTCA**	
		Molecule 1	Molecule 2			Molecule 1	Molecule 2	Molecule 1	Molecule 2
C(s)-C(o)-N-C(1r)	177.5(2)	177.3(3)	−176.8(3)	173.7(6)	−175.4(5)	−176.9(5)	173.0(5)	176.5(7)	−176.9(7)
C(o)-N-C(1r)-C(2r)	−109.9(2)	−112.2(4)	−68.4(5)	−111.4(7)	−117.9(6)	103.4(6)	75.9(6)	−78.8(1)	94.1(1)
C(o)-N-C(1r)-C(6r)	71.5(2)	68.0(5)	112.5(4)	69.2(9)	61.2(7)	−78.2(6)	−104.8(5)	100.3(1)	87.1(1)
O-C(o)-N-C(1r)	−3.1(3)	−1.2(6)	1.6(6)	−5.6(1)	2.1(9)	4.3(9)	−9.3(8)	−4.6(1)	1.9(1)
N-C(1r)-C(2r)-C(me)/Cl)	1.6(2)	−0.9(9)	−1.4(5)	−0.9(9)	−1.6(7)	−1.3(7)	−1.4(8)	−1.5(1)	−2.0(1)
N-C(1r)-C(6r)-C(me)/Cl)	−0.7(3)	1.2(5)	−1.9(5)	1.4(1)	4.2(7)	2.4(7)	2.7(7)	2.0(1)	0.1(1)
N-C(1r)-C(2r)-C(3r)	−178.5(1)	179.0(3)	−178.8(3)	178.6(6)	178.6(5)	177.9(4)	178.3(5)	175.9(8)	177.5(8)
N-C(1r)-C(6r)-C(5r)	178.5(2)	−178.9(3)	178.2(3)	−178.3(6)	−177.5(5)	−178.2(5)	−178.7(4)	−178.7(8)	177.9(7)
C(me)/Cl(1)-C(s)-C(o)-O	–	−14.5(6)	24.1(6)	79.5(7)	31.3(7)	−122.9(5)	−102.6(5)	'side chain	−44.3(1)
C(me)/Cl(2)-C(s)-C(o)-O	–	–	–	−41.2(9)	−90.2(6)	−1.9(7)	17.8(7)	Cl atoms	−164.7(7)
C(me)/Cl(3)-C(s)-C(o)-O	–	–	–	–	–	120.0(5)	138.3(5)	found at four	74.0(9)
C(me)/Cl(1)-C(s)-C(o)-N	–	166.9(4)	−157.4(4)	−99.8(6)	−151.1(4)	58.3(6)	75.3(5)	positions	134.6(7)
C(me)/Cl(2)-C(s)-C(o)-N	–	–	–	139.4(5)	87.5(5)	179.3(4)	−164.4(4)	each'	14.2(1)
C(me)/Cl(3)-C(s)-C(o)-N	–	–	–	–	–	−58.8(6)	−43.8(6)		−107.1(7)

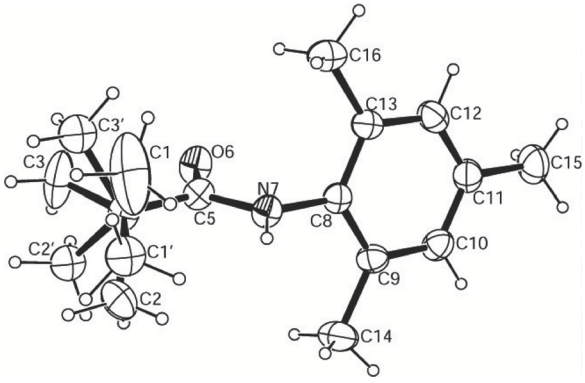

Fig. 2. Molecular geometry of *N*-(2,4,6-trimethylphenyl)-2,2,2-trimethyl-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$C(CH_3)_3$ (**TMPTMA**), with the numbering of atoms.

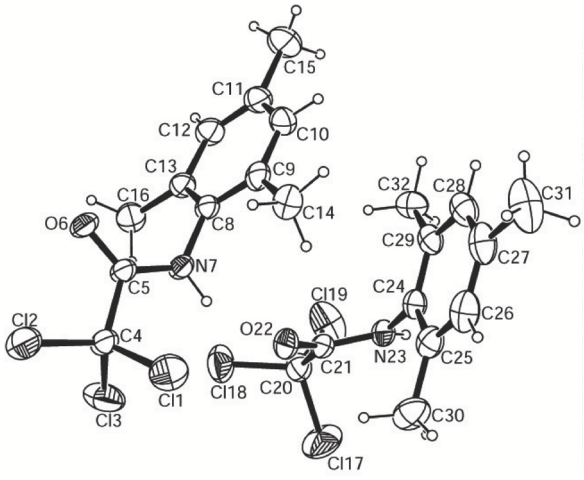

Fig. 3. Molecular geometry of *N*-(2,4,6-trimethylphenyl)-2,2,2-trichloro-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CCl_3 (**TMPTCA**), with the numbering of atoms.

ylphenyl)-2,2,2-trimethyl-acetamide and *N*-(2,4,6-trimethylphenyl)-2,2,2-trichloro-acetamide. Figures 1, 2 and 3 show the molecules of the title compounds as they appear in suitable projection with the numbering of the atoms used throuhout the paper. The projection of the typical unit cell of one of the compounds, **PTMA** is shown in Figure 4.

The compounds **PTMA**, and **TMPTMA** have 1 molecule each in their asymmetric units, similar to **PA**, **PTCA**, **TMPA**, **TMPDMA**, **TMPDCA**, **TCPA** and **TCPDCA**, while **TMPTCA** has 2 molecules in its asymmetric unit, similar to 2 molecules each in the asymmetric units of the compounds **TMPMA**, **TMPCA**, **TCPCA** and**TCPTCA**. If the compound **TCPMA** also has 2 molecules in its asymmetric unit, then it can be generalized that the amides **TMPMA**, **TMPCA**, **TCPMA**, **TCPCA**, **TMPTCA** and **TCPTCA** formed by the replacement of 1 or all the three H-atoms by -CH_3 or -Cl in either **TMPA** or **TCPA** leads to a solid state geometry with 2 molecules each in their asymmetric units, while **PA** (both the ring and side chain are unsubstituted), **PTMA** and **PTCA** (obtained by replacing all the 3 H-atoms in **PA** by -CH_3 or -Cl, respectively), **TMPA** and**TCPA** (obtained by 2-4-6-trimethyl or trichloro substitution in the benzene ring of **PA**, respectively), **TMPDMA** and **TMPDCA** (obtained by replacing 2 H-atoms in **TMPA** by -CH_3 or -Cl, respectively) and **TCPDCA** (obtained by replacing 2 H-atoms in **TCPA**

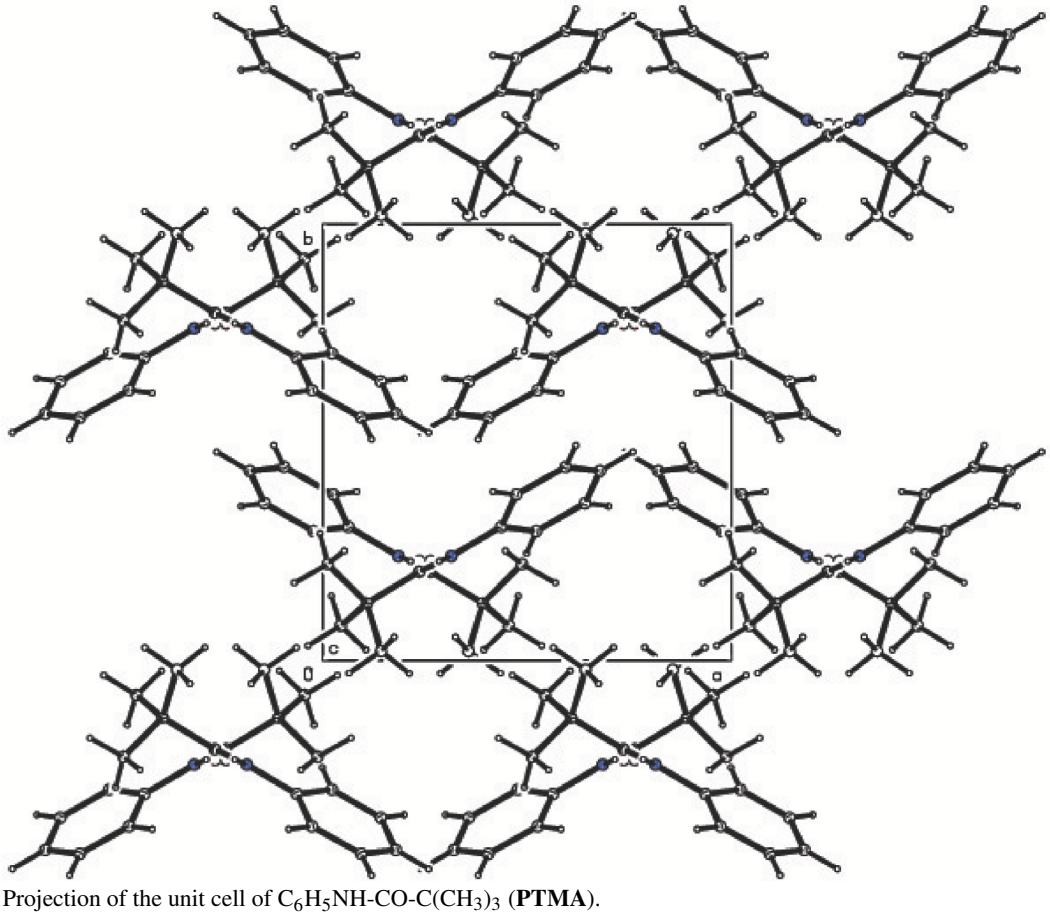

Fig. 4. Projection of the unit cell of C_6H_5NH-CO-$C(CH_3)_3$ (**PTMA**).

by -Cl) have one molecule each in their asymmetric units.

An is evident from the comparison of data in Table 3, conversion of **PA** into **TMPA** and**TCPA** by replacing 3 H-atoms at the 2nd, 4th and 6th position by -CH_3 or -Cl changes the crystal geometry from orthorhombic to monoclinic with the same *Z* number. But the introduction of Cl and CH_3 groups into the side chain will have different effects. The conversion of **PA** into **PTCA** by replacing the 3 H-atoms in the side chain by 3 Cl-atoms also changes over to the monoclinic system but with different space groups and *Z* numbers. But the conversion of **PA** into **PTMA** by replacing the 3 H-atoms in the side chain by -CH_3 does not lead to a change in the crystal geometry, only the space group and the *Z* number are changed. In other words, the conversion of **PA** into either **PTCA** or **TCPA** by substitution as above would lead to the monoclinic system with different space groups and *Z* numbers. But the conversion of **PA** into either **PTMA** or **TMPA** by substitution in either the side chain or the benzene ring will have different effects.

The conversion of **PTCA** into **TMPTCA** by introducing 3 CH_3-groups at the 2nd, 4th and 6th position will not change the crystal system but only changes the space group and *Z* number, while the conversion of **PTCA** into **TCPTCA** by introducing 3 Cl-atoms also at the 2nd, 4th and 6th position in the benzene ring changes the crystal system from monoclinic to triclinic. The conversion of **PTMA** into **TMPTMA** by introducing 3 CH_3-groups at the 2nd, 4th and 6th position also changes the crystal system from orthorhombic to tetragonal. Other changes in the crystal parameters with the successive replacement of H-atoms in the side chain by -CH_3 or -Cl at the 2nd, 4th and 6th position in the benzene ring are shown in Table 3. But the complete generalization requires structure determinations with varying mono- and di-ring substitutions

along with changes in the side chain with either electron withdrawing or donating groups. Our work in this direction is in progress.

The comparison of mean ring distances, along with the observed minimum and maximum distances and other bond distances for 14 compounds is also given in Table 3. The minimum and maximum mean ring distances are observed at 1.375 Å and 1.389 Å for **TCPTCA** and **TMPA**, respectively. The longest ring distance is observed at 1.413 Å for **PA**, which is both ring and side chain unsubstituted, while the shortest ring distance is observed at 1.350 Å for **TCPTCA**. **TCPTCA** is an amide with trichloro substitutions in both the benzene ring and the side chain. Chloro substitutions will have a relatively more pronounced effect on the crystal geometry, than the methyl groups.

The minimum and maximum C(ring)-N distances are observed at 1.410 Å and 1.439 Å for **TCPCA** and **TMPTCA**, respectively, while the minimum and maximum N-C(O) distances are observed at 1.316 Å and 1.357 Å for **TCPDCA** and **TCPA**, respectively. 1.193 Å and 1.235 Å are the minimum and maximum C-O distances for **TCPTCA** and **TCPDCA**, respectively, while the minimum and maximum C(O)-C(side) bond lengths are observed at 1.476 Å and 1.564 Å for **PA** and **PTCA**, respectively.

As regards the bond angles, the minimum and maximum C(2r)-C(1r)-C(6r) bond angles occur at 116.5° and 122.9° for **TCPCA** and **TMPTCA**, 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 119.9° (**TCPTCA**) and 129.3° (**PA**); 113.1° (**TMPDCA**) and 117.7° (**PA**); 121.4° (**TMPTMA**) and 126.3° (**PTCA**); 118.9° (**PTCA**) and 122.7° (**TCPCA**).

The comparison of available significant torsional 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 torsional angles C(s)-C(o)-N-C(1r) are higher by about 2° for the ring chloro substituted compounds than the ring methyl substituted compounds. As can be seen, the other torsional angles also undergo changes to different extents depending on the nature of substituent and the position of substitution.

The comparison of the bond parameters revealed that there are significant changes in them with substitution either in the benzene ring or in the side chain of the amides. But to draw further general conclusions substantive data are to be collected with varying substitutions. Our work in this direction is in progress.

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