Structural Studies on *N*-(2,4,6-Trimethylphenyl)-methyl/ chloro-acetamides, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH_{3-y}X_y$ (X = CH_3 or Cl and y = 0, 1, 2)

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Z. Naturforsch. **61a,** 588 – 594 (2006); received July 6, 2006

The effect of substitutions in the ring and in the side chain on the crystal structure of *N*-(2,4,6-trimethylphenyl)-methyl/chloro-acetamides of the configuration 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH_{3-y}X_y$ (X = CH_3 or Cl and $y = 0,1,2$) has been studied by determining the crystal structures of *N*-(2,4,6-trimethylphenyl)-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3 (**TMPA**); *N*-(2,4,6-trimethylphenyl)-2-methylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3 (**TMPMA**); *N*-(2,4,6-trimethylphenyl)-2,2-dimethylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH(CH_3)_2$ (**TMPDMA**) and *N*-(2,4,6-trimethylphenyl)-2,2-dichloroacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$ (**TMPDCA**). The crystallographic system, space group, formula units and lattice constants in Å are: **TMPA**: monoclinic, *Pn*, $Z = 2$, $a = 8.142(3)$, $b = 8.469(3)$, $c = 8.223(3)$, $\beta = 113.61(2)^\circ$; **TMPMA**: monoclinic, $P2_1/n$, $Z = 8$, $a = 9.103(1)$, $b = 15.812(2)$, $c = 16.4787(19)$, $\alpha = 89.974(10)^\circ$, $\beta = 96.951(10)^\circ$, $\gamma = 89.967(10)^\circ$; **TMPDMA**: monoclinic, $P2_1/c$, $Z = 4$, $a = 4.757(1)$, $b = 24.644(4)$, $c = 10.785(2)$, $\beta = 99.647(17)^\circ$; **TMPDCA**: triclinic, $P1$, $Z = 2$, $a = 4.652(1)$, $b = 11.006(1)$, $c = 12.369(1)$, $\alpha = 82.521(7)^\circ$, $\beta = 83.09(1)^\circ$, $\gamma = 79.84(1)^\circ$. The results are analyzed along with the structural data of *N*-phenylacetamide, C_6H_5NH-CO-CH_3; *N*-(2,4,6-trimethylphenyl)-2-chloroacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2Cl; *N*-(2,4,6-trichlorophenyl)-acetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-CH_3; *N*-(2,4,6-trichlorophenyl)-2-chloroacetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-CH_2Cl; *N*-(2,4,6-trichlorophenyl)-2,2-dichloroacetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-$CHCl_2$ and *N*-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-CCl_3. **TMPA**, **TMPMA** and **TMPDCA** have one molecule each in their asymmetric units, while **TMPDMA** has two molecules in its asymmetric unit. Changes in the mean ring distances are smaller on substitution as the effect has to be transmitted through the peptide linkage. The comparison of the other bond parameters reveal that there are significant changes in them on substitution.

Key words: Crystal Structures; *N*-(2,4,6-Trimethylphenyl)-methyl/chloro-acetamides.

1. Introduction

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. Thus 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. Many acetanilides also exhibit fungicidal and herbicidal activities. This has further stimulated interest in their chemistry. Thus we are interested in the spectroscopic and structural characteristics of this class of compounds [1 – 10]. The objective is to see how the -NHCO- bond parameters vary with substitution both in the benzene ring and in the side chain. As part of continuing studies in this direction, we report herein the structural studies on *N*-(2,4,6-trimethylphenyl)-methyl / chloro-acetamides of the configuration 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH_{3-y}X_y$ (X = CH_3 or Cl and $y = 0,1,2$). The crystal structures of *N*-(2,4,6-trimethylphenyl)-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3 (**TMPA**); *N*-(2,4,6-trimethylphenyl)-2-methylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3 (**TMPMA**); *N*-(2,4,6-trimethylphenyl)-2,2-dimethylacetamide, 2,4,6-$(CH_3)_3$-

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of *N*-(2,4,6-trimethylphenyl)-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3 (**TMPA**); *N*-(2,4,6-trimethylphenyl)-2-methylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3 (**TMPMA**); *N*-(2,4,6-trimethylphenyl)-2,2-dimethylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH(CH_3)_2$ (**TMPDMA**) and *N*-(2,4,6-trimethylphenyl)-2,2-dichloroacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$ (**TMPDCA**). Diffractometer: Stoe-Stadi4 (Mo-K_α); monochromator: graphite (002); scan $\omega/2\theta = 1/1$; refinement method: full-matrix least-squares on F^2.

Description	**TMPA**	**TMPMA**	**TMPDMA**	**TMPDCA**
Chemical formula	$C_{11}H_{15}NO$	$C_{12}H_{17}NO$	$C_{13}H_{19}NO$	$C_{11}H_{13}Cl_2NO$
Formula mass, g mol^{-1}	177.24	191.27	205.29	246.12
Temperature, K	304(2)	293(2)	304(2)	299(2)
Wavelength, pm	71.073	71.073	71.069	154.180
Crystal system	monclinic	monoclinic	monoclinic	triclinic
Space group	Pn	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a, Å	8.142(3)	9.103(1)	4.757(1)	4.652(1)
b, Å	8.469(3)	15.812(2)	24.644(4)	11.006(1)
c, Å	8.223(3)	16.4787(19)	10.785(2)	12.369(1)
α, deg.	90	89.974(10)	90	82.521(7)
β, deg.	113.61(2)	96.951(10)	99.647(17)	83.09(1)
γ, deg.	90	89.967(10)	90	79.84(1)
Volume, Å^3	519.6(3)	2354.6(5)	1246.4(4)	615.0(1)
Z	2	8	4	2
Density (calculated), g cm^{-3}	1.133	1.079	1.094	1.329
Absorption coefficient, cm^{-1}	0.72	0.68	0.69	45.38
$F(000)$	192	832	448	256
Crystal size, mm^3	$0.51 \times 0.24 \times 0.14$	$0.20 \times 0.215 \times 0.55$	$0.55 \times 0.19 \times 0.11$	$0.32 \times 0.08 \times 0.03$
θ Range, deg.	2.40 to 26.05	4.12 to 26.37	1.65 to 26.08	9.37 to 56.91
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 10$, $-10 \le l \le 4$	$-9 \le h \le 11$, $-19 \le k \le 19$, $-20 \le l \le 20$	$-5 \le h \le 1$, $0 \le k \le 30$, $-13 \le l \le 13$	$-5 \le h \le 1$, $-11 \le k \le 11$, $-13 \le l \le 13$
Reflections collected	3347	14813	2912	1860
Independent reflections	1663	4746	2466	1618
R(int)	0.0156	0.1018	0.0187	0.1686
Completeness to 2θ	99.8%	98.4%	97.4%	98.7%
Max. and min. transmission	–	–	0.9924 and 0.9632	0.8759 and 0.3245
Absorption correction	analytical	FACE	empiric-psi-scans	analytical
Data	1663	4746	2466	1618
Restraints/parameters	2/126	0/262	0/146	0/142
Goodness-of-fit on F^2	1.057	0.916	1.048	1.030
Final $R\,[I > 2\theta(I)]$	$R1 = 0.0354$, $wR2 = 0.0970$	$R1 = 0.0839$, $wR2 = 0.1968$	$R1 = 0.0549$, $wR2 = 0.1385$	$R1 = 0.0765$, $wR2 = 0.1779$
R Indices (all data)	$R1 = 0.0387$, $wR2 = 0.1009$	$R1 = 0.2039$, $wR2 = 0.2426$	$R1 = 0.0944$, $wR2 = 0.1696$	$R1 = 0.1499$, $wR2 = 0.2125$
Absolute structure parameter	$-1.4(17)$	–	–	–
Extinction coefficient	0.071(10)	0.061(7)	0.014(3)	0.0048(19)
Largest diff. peak and hole, e Å^{-3}	0.098 and −0.123	0.300 and −0.230	0.211 and −0.194	0.343 and −0.314

C_6H_2NH-CO-$CH(CH_3)_2$ (**TMPDMA**) and *N*-(2,4,6-trimethylphenyl)-2,2-dichloroacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$ (**TMPDCA**) have been determined and the data analyzed along with the structures of *N*-phenylacetamide, C_6H_5NH-CO-CH_3 (**PA**), *N*-(2,4,6-trimethylphenyl)-2-chloroacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2Cl (**TMPCA**); *N*-(2,4,6-trichlorophenyl)-acetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-CH_3(**TCPA**); *N*-(2,4,6-trichlorophenyl)-2-chloroacetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-CH_2Cl (**TCPCA**); *N*-(2,4,6-trichlorophenyl)-2,2-dichloroacetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-$CHCl_2$ (**TCPDCA**) and *N*-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide, 2,4,6-$Cl_3C_6H_2NH$-CO-CCl_3 (**TCPTCA**) [9, 11, 12].

2. Experimental

2.1. Preparation and Characterization of Compounds

The compounds **TMPA**, **TMPMA**, **TMPDMA** and **TMPDCA** were prepared from 2,4,6-trimethylaniline

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \cdot 10^3$) of *N*-(2,4,6-trimethylphenyl)-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3 ; *N*-(2,4,6-trimethylphenyl)-2-methylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3; *N*-(2,4,6-trimethylphenyl)-2,2-dimethylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH(CH_3)_2$ and *N*-(2,4,6-trimethylphenyl)-2,2-dichloroacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$. *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)
2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3:				
C(1)	5082(2)	8402(2)	3835(2)	46(1)
C(2)	4553(2)	6910(2)	4179(2)	47(1)
C(3)	4260(2)	5725(2)	2925(3)	53(1)
C(4)	4478(2)	5974(2)	1362(3)	53(1)
C(5)	4995(2)	7469(2)	1064(3)	57(1
C(6)	5305(2)	8690(2)	2272(2)	53(1)
C(8)	4389(2)	10878(2)	4959(2)	50(1)
C(9)	4964(3)	11955(2)	6531(3)	64(1)
C(10)	4305(3)	6603(2)	5854(3)	63(1)
C(11)	4200(3)	4659(3)	44(3)	73(1)
C(12)	5894(4)	10283(3)	1890(3)	77(1)
N(7)	5425(2)	9608(2)	5141(2)	49(1)
O(13)	3064(2)	11171(2)	3608(2)	69(1)
2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3:				
C(1)	−4772(3)	5757(2)	1916(2)	56(1)
C(2)	−4781(4)	4887(2)	1830(2)	58(1)
C(3)	−3906(4)	4419(2)	2401(3)	72(1)
C(4)	−3015(5)	4791(3)	3042(3)	81(1)
C(5)	−3076(5)	5653(3)	3115(3)	86(1)
C(6)	−3933(4)	6153(3)	2563(2)	68(1)
C(8)	−5113(4)	6775(2)	795(2)	58(1)
C(9)	−6232(4)	7210(3)	196(3)	85(1)
C(10)	−5651(6)	7899(4)	−239(4)	138(2)
C(11)	−5695(4)	4468(3)	1131(2)	82(1)
C(12)	−2035(5)	4255(3)	3662(3)	115(2)
C(13)	−3931(5)	7091(3)	2679(3)	102(2)
C(15)	171(4)	7432(2)	1187(2)	56(1)
C(16)	1113(4)	7628(3)	1892(2)	64(1)
C(17)	1861(4)	8392(3)	1926(3)	80(1)
C(18)	1696(4)	8966(3)	1296(3)	82(1)
C(19)	750(4)	8744(3)	599(3)	78(1)
C(20)	−9(4)	7992(2)	528(2)	60(1)
C(22)	−50(4)	5897(2)	1100(2)	57(1)
C(23)	−1127(4)	5176(3)	1003(3)	80(1)
C(24)	−521(5)	4359(3)	1272(3)	106(2)
C(25)	1285(5)	7055(3)	2621(2)	93(1)
C(26)	2451(6)	9809(3)	1375(4)	132(2)
C(27)	−998(4)	7786(3)	−240(3)	86(1)
O(14)	−3779(2)	6881(2)	788(2)	76(1)
O(28)	1282(2)	5784(2)	1126(2)	80(1)
N(7)	−5665(3)	6259(2)	1317(2)	60(1)
N(21)	−631(4)	6668(2)	1136(2)	63(1)
2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH(CH_3)_2$:				
C(1)	−1388(4)	3942(1)	2959(2)	45(1)
C(2)	−2691(4)	4192(1)	1855(2)	49(1)
C(3)	−1802(5)	4711(1)	1595(2)	57(1)
C(4)	316(5)	4982(1)	2394(3)	61(1)
C(5)	1504(6)	4726(1)	3488(3)	65(1)
C(6)	688(5)	4209(1)	3803(2)	55(1)
C(8)	−503(4)	2971(1)	3212(2)	51(1)
C(9)	−1812(4)	2421(1)	3373(3)	56(1)
C(10)	−2801(8)	2172(1)	2098(3)	94(1)
C(11)	269(6)	2058(1)	4200(3)	79(1)
C(12)	−4994(5)	3911(1)	959(3)	66(1)
C(13)	1279(8)	5542(1)	2064(3)	87(1)
C(14)	2049(7)	3960(1)	5029(3)	78(1)
N(7)	−2223(4)	3402(1)	3220(2)	49(1)
O(15)	1983(3)	3015(1)	3066(2)	77(1)
2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$:				
C(1)	5802(12)	7704(6)	2080(4)	35(2)
C(2)	7217(12)	6631(6)	1634(5)	38(2)
C(3)	6627(14)	6471(7)	577(5)	48(2)
C(4)	4754(15)	7340(7)	−5(5)	47(2)
C(5)	3440(15)	8396(7)	466(5)	49(2)
C(6)	3946(13)	8611(7)	1506(5)	41(2)
C(8)	4312(13)	7810(6)	4018(5)	40(2)
C(9)	5490(13)	7848(7)	5116(5)	44(2)
C(10)	9288(15)	5659(7)	2245(6)	55(2)
C(11)	4110(20)	7147(8)	−1136(6)	71(2)
C(12)	2461(17)	9805(7)	1961(6)	64(2)
N(7)	6354(11)	7853(5)	3170(4)	35(1)
O(13)	1791(9)	7736(6)	3969(4)	71(2)
Cl(14)	6129(6)	6339(3)	5767(2)	100(1)
Cl(15)	2878(4)	8813(3)	5925(2)	86(1)

and the substituted chloroacetylchlorides or substituted acetic acids (Aldrich, Germany) and phosphoryl chloride or thionyl chloride [9, 13]. The commercial 2,4,6-trimethylaniline and 2,2-dichloroacetic acid were purified by double distillation. All other reagents employed in the preparations and purifications of the compounds were of analytical grade. The compound **TMPA** was prepared from 2,4,6-trimethylaniline and acetyl chloride in benzene, while **TMPMA**, **TMPDMA** and **TMPDCA** were prepared by treating 2,4,6-trimethylaniline, respectively, with a clear mixture of 2-methylacetic acid, 2,2-dimethylacetic acid and 2,2-dichloroacetic 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 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

Table 3. Comparison of crystal structure data of *N*-(2,4,6-trimethylphenyl/trichlorophenyl)-methyl/chloro-acetamides.

Parameter	**PA**	**TMPA**	**TMPMA**	**TMPDMA**	**TMPCA**	**TMPDCA**	**TCPA**	**TCPCA**	**TCPDCA**	**TCPTCA**
Crystal system	ortho-rhombic	mono-clinic	mono-clinic	mono-clinic	mono-clinic	tri-clinic	mono-clinic	ortho-rhombic	ortho-rhombic	tri-clinic
Space group	*Pbca*	*Pn*	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	*Pn*	$Pna2_1$	$P2_12_12$	$P\bar{1}$
Z	8	2	8	4	8	2	2	8	4	4
Bond lengths:										
C(ring)-N	1.426	1.427	1.424	1.429	1.427	1.437	1.413	1.410	1.417	1.432
N-C(O)	1.330	1.337	1.330	1.343	1.320	1.330	1.357	1.345	1.316	1.332
C-O	1.226	1.225	1.224	1.224	1.231	1.199	1.221	1.216	1.235	1.193
C(O)-C(side)	1.476	1.495	1.498	1.513	1.510	1.532	1.499	1.513	1.511	1.531
Bond angles:										
C(2r)-C(1r)-C(6r)	121.2	120.7	121.2	121.1	121.5	122.0	117.3	116.5	117.4	118.1
C(2r)-C(1r)-N	115.7	118.6	119.5	118.8	118.9	117.7	120.1	121.7	121.1	119.5
C(6r)-C(1r)-N	122.7	120.8	119.3	120.1	119.7	120.2	122.5	121.9	121.4	122.4
C(1r)-N-C(O)	129.3	124.6	124.7	123.1	123.9	122.4	123.2	123.0	124.4	119.9
N-C(O)-C(side)	117.7	115.4	115.8	116.5	114.7	113.1	114.8	113.9	115.4	116.0
N-C(O)-O	121.7	123.4	122.5	122.2	124.0	125.4	123.2	123.5	124.4	124.9
O-C(O)-C(side)	120.4	121.2	121.8	121.3	121.3	121.4	122.0	122.7	120.1	119.3

Table 4. Comparison of significant dihedral angles (degree) (standard deviations) of some *N*-(2,4,6-trimethylphenyl/trichlorophenyl)-methyl/chloro-acetamides.

Connection	Angle				
	TMPA	**TMPMA**		**TMPDCA**	**TCPDCA**
		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)
C(O)-N-C(1r)-C(2r)	−109.9(2)	−112.2(4)	−68.4(5)	−111.4(7)	−117.9(6)
C(O)-N-C(1r)-C(6r)	71.5(2)	68.0(5)	112.5(4)	69.2(9)	61.2(7)
O-C(O)-N-C(1r)	−3.1(3)	−1.2(6)	1.6(6)	−5.6(1)	2.1(9)
N-C(1r)-C(2r)-C(me/Cl)	1.6(2)	−0.9(9)	−1.4(5)	−0.9(9)	−1.6(7)
N-C(1r)-C(6r)-C(me/Cl)	−0.7(3)	1.2(5)	−1.9(5)	1.4(1)	4.4(7)
C(me)/Cl(1)-C(s)-C(O)-O	–	−14.5(6)	24.1(6)	79.5(7)	31.3(7)
C(me)/Cl(2)-C(s)-C(O)-O	–	–	–	−41.2(9)	−90.2(6)
C(me)/Cl(1)-C(s)-C(O)-N	–	166.9(4)	−157.4(4)	−99.8(6)	−151.1(4)
C(me)/Cl(2)-C(s)-C(O)-N	–	–	–	139.4(5)	87.5(5)

TMPA, **TMPMA**, **TMPDMA** and **TMPDCA** was checked by determining their melting points. The melting points (in °C) are: **TMPA**, 212; **TMPMA**, 154; **TMPDMA**, 148; **TMPDCA**, 160. The compounds were further characterized by recording their infrared spectra and comparing the frequencies with the literature values [9].

2.2. Crystal Structure Studies

Good single crystals of **TMPA**, **TMPMA**, **TMPDMA** and **TMPDCA** 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) [14 – 22]. 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, and to 0.98 Å for the $CHCl_2$ group. Further experimental conditions for structure determinations and refinements are given in Table 1.

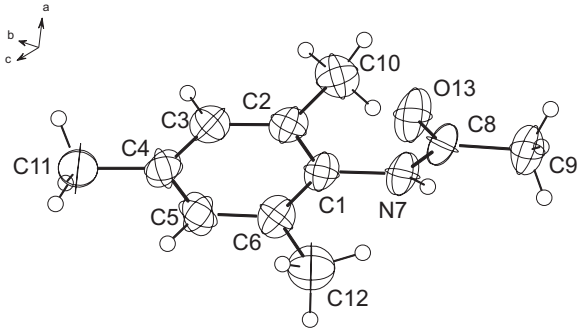

Fig. 1. Molecular geometry of *N*-(2,4,6-trimethylphenyl)-acetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_3 (**TMPA**), with the numbering of atoms.

3. Results and Discussion

The crystallographic data for the compounds, **TMPA**, **TMPMA**, **TMPDMA** and **TMPDCA** are

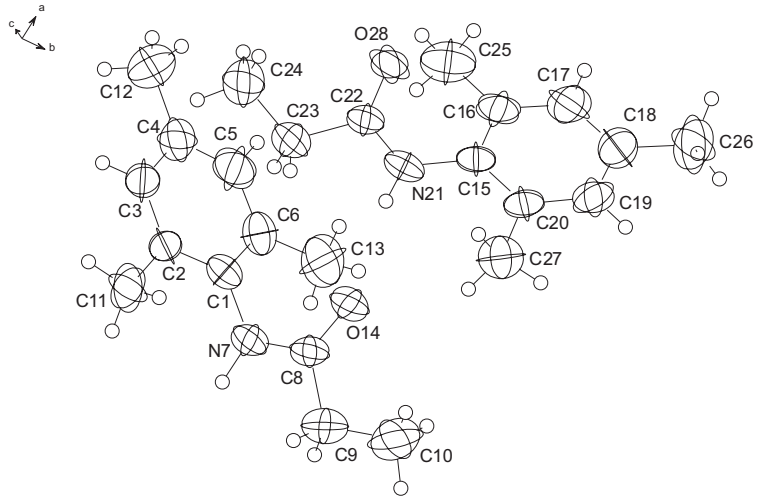

Fig. 2. Molecular geometry of *N*-(2,4,6-trimethylphenyl)-2-methylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-CH_2CH_3 (**TMPMA**), with the numbering of atoms.

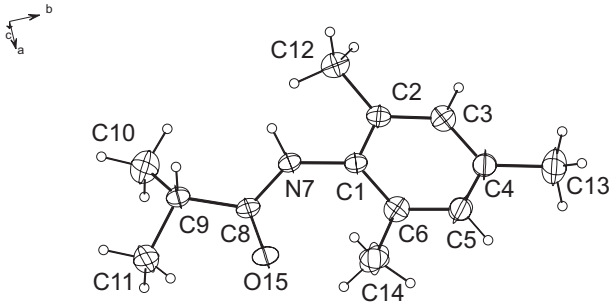

Fig. 3. Molecular geometry of *N*-(2,4,6-trimethylphenyl)-2,2-dimethylacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CH(CH_3)_2$ (**TMPDMA**), with the numbering of atoms.

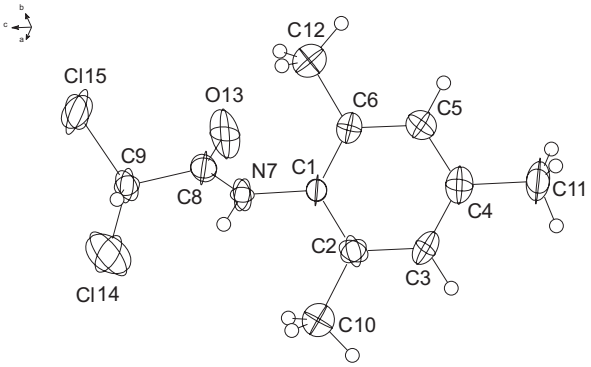

Fig. 4. Molecular geometry of *N*-(2,4,6-trimethylphenyl)-2,2-dichloroacetamide, 2,4,6-$(CH_3)_3C_6H_2NH$-CO-$CHCl_2$ (**TMPDCA**), with the numbering of atoms.

given in Table 1. The atomic coordinates and the mean displacement parameters are listed in Table 2. In Table 3, the significant bond distances, bond angles and other structural data of these compounds are compared together with those of **PA**, **TMPCA**, **TCPA**, **TCPCA**, **TCPDCA** and **TCPTCA**. Table 4 lists selected dihedral angles for the compounds **TCPDCA** and **TMPDCA**. The hydrogen coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations 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 239744, 610288, 239745 and 610167, respectively, for *N*-(2,4,6-trimethylphenyl)-acetamide, *N*-(2,4,6-trimethylphenyl)-2-methylacetamide, *N*-(2,4,6-trimethylphenyl)-2,2-dimethyl-acetamide and *N*-(2,4,6-trimethylphenyl)-2,2-dichloroacetamide. Figures 1 to 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 the 50% probability level.

The compounds **TMPA**, **TMPMA** and **TMPDCA** show one molecule each in their asymmetric units, while **TMPDMA** shows two molecules in its asymmetric unit, compared to two molecules each in the asymmetric units of the compounds **TMPCA** and **TCPCA**. First we shall discuss the intramolecular geometry of the four title compounds (Table 3). The average bond distances of C(*i*)-C(*j*) within the benzene rings of the four compounds in ångstrom units are as follows. The observed minimum and maximum bond lengths in Å are given in parentheses: 1.389

(1.382, 1.400); 1.382 (1.371, 1.396); 1.386 (1.372, 1.391); 1.386 (1.359, 1.401); 1.387 (1.368, 1.406) Å for **TMPA**, **TMPMA**, **TMPDMA**, **TMPCA** and **TMPDCA**, respectively, compared to 1.384 (1.374, 1.398); 1.381 (1.361, 1.399); 1.378 (1.355, 1.390) and 1.375 (1.350, 1.401) Å for the compounds **TCPA**, **TCPCA**, **TCPDCA** and **TCPTCA**, respectively. As may be seen, the mean ring distances are generally slightly larger for methyl substituted compounds than the corresponding chloro substituted compounds, 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 gradual replacement of H atoms by Cl atoms in the side chain of the trichlorophenyl compounds slightly decreases the mean ring distances in these compounds, while the effect does not show a trend with triphenyl substituted compounds. Changes in the mean ring distances due to changes in the side chain are smaller, as the effect has to be transmitted through the peptide linkage. The other bond lengths are compared in Table 3. As may be seen, the introduction of 3 methyl groups in the benzene ring of the substituted acetamide does not significantly affect the C1(ring)-N distance, while the introduction of 3 Cl atoms changes the distance by about 0.01 Å. The N-C(O) bond variation with methyl group substitution to the benzene ring does not show a trend, while the introduction of 3 Cl atoms increases the distance by about 0.03 Å. The latter gets lowered as the number of Cl atoms increase in the side chain. The variation of the C-O distance does not show a trend on substitution of either the methyl groups or Cl atoms either in the ring or in the side chain. But the C(O)-C(side chain) distance is generally increased by 0.02 to 0.06 Å on introduction of either the methyl groups or Cl atoms to the benzene ring.

As regards the ring bond angles, they are observed between 117.7° and 122.4° (**TMPA**), 117.1° and 122.8° (**TMPMA**), 117.7° and 122.6° (**TMPDMA**), 117.2° and 123.2° (**TMPCA**), 117.8° and 122.7° (**TMPDCA**), compared to the bond angles observed between 117.3° and 122.1° (**TCPA**), 116.5° and 123.2° (**TCPCA**), 117.4° and 122.3° (**TCPDCA**) 118.0° and 122.2° (**TCPTCA**) for the trichlorophenyl substituted acetamides. The comparison of other bond angles are shown in Table 3. Introduction of methyl groups in the benzene ring does not significantly alter the C(2ring)-C(1ring)-C(6ring) bond angles, while the introduction of Cl atoms changes it by 3° to 5°. The addition of methyl groups to the benzene ring lowers the C(6ring)-C(1ring)-N angles by 2° to 3°, while the addition of Cl atoms has a marginal effect. The methyl group substitution increases the C(2ring)-C(1ring)-N bond angle by 2° to 4°, while the addition of Cl atoms increases it by 4° to 6°. The C(ring)-N-C(O) bond angle is greatly affected, by 5° to 10° on substitution. The substitution also alters the N-C(O)-C(side chain) bond angle by 2° to 4.5°, but with no regular trend. The N-C(O)-O bond angle is altered by 0.5° to 4° with substitution.

The comparison of selected dihedral angles is shown in Table 4. It is evident from the data that there are changes in them on ring and side chain modifications.

4. Conclusions

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 general conclusions, further substantive data are to be collected with varying substitutions. Our work in this direction is in progress.

Acknowledgements

B. T. G. thanks the Alexander von Humboldt Foundation, Bonn, Germany for resumption of his research fellowship. J. K. thanks the Grant Agency of the Slovak Republic (Grant No. 1/2449/05).

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