Structural Studies on N-(2,4,5-trichlorophenyl)-2-Chloro- and 2,2,2-trichloroacetamides and N-Chloro-N-(2,4,5-trichlorophenyl)-2-Chloroacetamide

B. Thimme Gowda, I. Svoboda[a], and Hartmut Fuess[a]

Department of Studies in Chemistry, Mangalore University,
Mangalagangotri-574 199, Mangalore, India
[a] Darmstadt University of Technology, Institute of Materials Science, Petersenstr.23,
D-64287 Darmstadt, Germany

Reprint requests to Prof. B. T. G.; Fax: +91 824 2287 367; E-mail: gowdabt@yahoo.com or
Prof. H. F.; Fax: +49 6151 16 60 23; E-mail: hfuess@tu-darmstadt.de

Z. Naturforsch. **59a,** 845 – 852 (2004); received June 28, 2004

The effect of N-chloro, side chain and sites of ring substitutions on the crystal structure of N-(trichlorophenyl)-2-chloro and 2,2,2-trichloroacetamides has been studied by determining the crystal structure of N-(2,4,5-trichlorophenyl)-2-chloroacetamide, 2,4,5-$Cl_3C_6H_2$.NHCO.CH_2Cl (N245TCPCA), N-chloro-N-(2,4,5-trichlorophenyl)-2-chloroacetamide, 2,4,5-$Cl_3C_6H_2$.NClCO.CH_2Cl (NC245TCPCA) and N-(2,4,5-trichlorophenyl)-2,2,2-trichloroacetamide, 2,4,5-$Cl_3C_6H_2$.NHCO.CCl_3 (N245TCPTCA). The crystal type, space group, formula units and lattice constants in Å are: **N245TCPCA:** monoclinic, $P2_1/n$, $Z = 4$, $a = 4.732(1)$, $b = 29.522(3)$, $c = 7.734(1)$, $\beta = 108.33(1)^\circ$; **NC245TCPCA:** monoclinic, $P2_1/c$, $Z = 4$, $a = 15.965(3)$, $b = 9.398(1)$, $c = 7.352(2)$, $\beta = 91.51(2)^\circ$; **N245TCPTCA:** orthorhombic, $Pmc2_1$, $Z = 4$, $a = 6.945(1)$, $b = 11.370(3)$, $c = 15.555(3)$. The results are compared with the structure of N-(phenyl)-acetamide, N-(phenyl)-2,2,2-trichloroacetamide, N-(2-chlorophenyl)-2,2,2-trichloroacetamide, N-(4-chlorophenyl)-2,2,2-trichloroacetamide, N-(2,6-dichlorophenyl)-2,2,2-trichloroacetamide, N-(2,4,6-trichlorophenyl)-acetamide, N-(2,4,6-trichlorophenyl)-2-chloroacetamide and N-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide. The comparison of the bond parameters reveal that there are significant changes by substitution in both the ring and side chain of the amides and by N-chlorination. But to draw general conclusions further, substantial work is needed with varying substitutions.

Key words: Crystal Structures; N-(2,4,5-trichlorophenyl)-chloroacetamides;
N-chloro-N-(2,4,5-trichlorophenyl)-2-chloroacetamide.

1. Introduction

Nuclear quadrupole resonance and crystal structural studies give valuable information on bond properties [1 – 4]. 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 [5, 6]. Thus we are interested in NQR and X-ray diffraction studies of amides in their crystalline state [7 – 15]. Pies, Rager, and Weiss [16] have studied ^{35}Cl NQR spectra of chloroacetanilides $Cl_xC_6H_{5-x}NHCOCH_{3-y}Cl_y$ and observed interesting trends in their spectra. We have reported ^{35}Cl NQR and IR spectra of a number of N-(chlorophenyl) chloroacetamides of the configuration: $X_yC_6H_{5-y}$-NHCO-$CH_{3-y}Cl_y$ (where X = CH_3, NO_2 or Br and $y = 1$, 2 or 3) [10 – 13]. Crystal structure of some of the N-phenyl acetamides and N-substituted phenyl chloroacetamides has also been determined [8, 9, 14, 15, 17 – 19]. We have recently studied the crystal structure of compounds of the type, 2,4,6-$X_3C_6H_2$·NHCO·$CH_{3-y}Cl_y$ (X = CH_3 or Cl and $1 \leq y \leq 3$) and analysed the data along with the crystal structure of the related compounds [20], to see how the -NHCO- bond parameters vary with the substitution of both the electron donating and electron withdrawing groups in the benzene ring and in the side chain. In the process we have observed that N-phenyl acetamide on conversion to either N-phenyl-2,2,2-trichloroacetamide **or** N-(2,4,6-trichlorophenyl)-acetamide by side chain or ring substitution changes its crystal symmetry from orthorhombic to monoclinic. But both

the side chain and ring substitutions of N-phenyl acetamide converts it into N-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide, and its orthorhombic symmetry is changed to triclinic. On conversion of N-phenyl-2,2,2-trichloroacetamide to N-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide via mono and di ring substitutions, the crystal symmetry changes from monoclinic to triclinic via orthorhombic and monoclinic symmetries, while conversion of N-(2,4,6-trichlorophenyl)-acetamide to N-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide via mono and di- side chain substitutions by Cl changes its crystal symmetry from monoclinic to triclinic through orthorhombic symmetries twice. Hence we thought it interesting to study the effect of changing the sites of Cl-substitutions from 2,4,6 to 2,4,5 in the phenyl ring and N-chlorination on the structural aspects of N-(trichlorophenyl)-chloroacetamides. We thus report herein the crystal structures of N-(2,4,5-trichlorophenyl)-2-chloroacetamide, 2,4,5-Cl_3 C_6H_2.NHCO.CH_2Cl (N245TCPCA), N-chloro-N-(2,4,5-trichlorophenyl)-2-chloroacetamide, 2,4,5-$Cl_3C_6H_2$.NClCO.CH_2Cl (NC245TCPCA) and N-(2,4,5-trichlorophenyl)-2,2,2-trichloroacetamide, 2,4,5-$Cl_3C_6H_2$.NHCO.CCl_3 (N245TCPTCA) and correlate with earlier studies.

2. Experimental

2.1. Preparation and Characterisation of the Compounds

The compounds N245TCPCA and N245TCPTCA were prepared from 2,4,5-trichloroaniline and the corresponding chloroacetylchloride or chloroacetic acid and phosphoryl chloride (Aldrich, Germany) [7, 9, 16, 21]. The commercial trichloroaniline was purified by zone refining. The compound N245TCPCA was prepared from 2,4,5-trichloroaniline and 2-chloroacetyl chloride in acetone (chemical analysis: % (found/calculated); C (62.25/62.41), H (6.52/6.67) and N (6.50/6.62)), while N245TCPTCA was prepared by treating 2,4,5-trichloroaniline with a homogeneous mixture of 2,2,2-trichloroacetic acid with phosphoryl chloride under constant stirring. The mixture was slowly warmed to expel HCl. Excess phosphoryl chloride was hydrolysed by adding cold water dropwise under ice cold conditions. The separated solids were filtered under suction, washed thoroughly with water and dried. The compounds were recrystallised from ethanol several times. The purity of the compounds N245TCPCA and N245TCPTCA was checked by determining their melting points. The melting points in °C are (the values in parentheses are literature values [16, 21]): (N245TCPCA) 180 (180) and (N245TCPTCA) 119 (118 – 120). The compounds were further characterised by recording their infrared and/or ^{35}Cl NQR spectra and comparing the frequencies with the literature values. All other reagents employed in the preperations and purification of compounds were of analytical grade.

2.2. Preparation of NC245TCPCA

It was prepared by treating acetic acid solution of N245TCPCA with an excess of aqueous acetic acid solution of calcium hypochlorite under vigorous stirring (1 hr). The organic matter was extracted with chloroform. The chloroform solution was further treated with a fresh aqueous acetic acid solution of calcium hypochlorite 2 – 3 times to ensure complete N-chlorination. Then the chloroform solution was freed from acetic acid using $NaHCO_3$ and then dried with anhydrous sodium sulphate. Chloroform was slowly evaporated at room temperature to obtain NC245TCPCA. The resulting compound was recrystallised from chloroform, toluene or cyclohexane. The purity of the compound was checked by estimating the amount of active chlorine content by iodometric titration and by recording its infrared spectrum.

2.3. Crystal Structure Studies

Small single crystals of N245TCPCA, NC245TC PCA and N245TCPTCA 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) [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 0.97 Å for the CH_2Cl group. Further experimental conditions for structure determinations and refinements are given in Table 1.

3. Results and Discussion

The crystallographic data of the compounds, N245TCPCA, NC245TCPCA and N245TCPTCA are given in Table 1. The atomic coordinates and the mean

Compound	GT16 N245TCPCA	GT12 NC245TCPCA	GT14 N245TCPTCA
Empirical formula	C8 H5 Cl4 N O	C8 H4 Cl5 N O	C8 H3 Cl6 N O
Formula weight	272.94	307.38	341.82
Temperature, K	301(2)	300(2)	301(2)
Wavelength, pm	71.093	71.093	71.093
Crystal system,	Monoclinic	Monoclinic	Orthorhombic
Space group	P21/n	P21/c	Pmc21
a, Å	4.732(1)	15.965(3)	6.945(1)
b, Å	29.522(3)	9.398(1)	11.370(3)
c, Å	7.734(1)	7.352(2)	15.555(3)
β, deg.	108.33(1)	91.51(2)	90
Volume, Å^3	1025.6(3)	1102.7(4)	1228.3(4)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.768	1.852	1.848
Abs. coeff., cm^{-1}	10.25	11.84	12.70
$F(000)$	544	608	672
Crystal size, mm^3	$1.25 \times 0.15 \times 0.05$	$1.00 \times 0.20 \times 0.15$	$1.00 \times 0.20 \times 0.15$
q range, deg.	1.38 to 25.97	1.28 to 25.97	1.79 to 25.96
Index ranges	$-5 \le h \le 3$, $-36 \le k \le 0$, $-9 \le l \le 9$	$-19 \le h \le 19$, $-11 \le k \le 0$, $-9 \le l \le 1$	$-8 \le h \le 3$, $-14 \le k \le 0$, $-19 \le l \le 19$
Refl. Coll.	3306	2374	3507
Indepen. Refl.	2017	2163	2603
[*R*(int)]	0.0526	0.0465	0.0166
Completeness to 2theta	25.97 98.0%	25.97 94.0%	25.96 100.0%
Absorption corr.	Empiric Psi-scan	None	None
Max.and min. transm.	0.8367 and 0.6501	–	0.8323 and 0.3632
Data	2017	2163	2603
Restraints/ parameters	0/130	0 / 136	1 / 188
Goodness-of-fit on F^2	1.043	1.091	1.059
Final *R*[I> 2s(I)]	$R1 = 0.0536$ $WR2 = 0.1435$	$R1 = 0.0315$ $wR2 = 0.0855$	$R1 = 0.0392$ $wR2 = 0.1071$
R indices (all data)	$R1 = 0.0740$ $WR2 = 0.1608$	$R1 = 0.0399$ $wR2 = 0.0893$	$R1 = 0.0460$ $wR2 = 0.1110$
Absol. str. Parameter	–	–	$-0.05(11)$
Extinction coefficient	–	–	0.0128(16)
Largest diff: (peak, hole), e.Å^3	0.433 and -0.939	0.392 and -0.353	0.629 and -0.488

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of 2,4,5-$Cl_3C_6H_2 \cdot NHCO \cdot CH_2Cl$ (**N245TCPCA**); 2,4,5-$Cl_3C_6H_2 \cdot NClCO \cdot CH_2Cl$ (**NC245TCPCA**) and 2,4,5-$Cl_3C_6H_2 \cdot NHCO \cdot CCl_3$ (**N245TCPTCA**).

Diffractometer: Nonius CAD 4; wavelength: 71.093 pm (MoK_α); Monochromator: Graphite (002); scan $\omega/2\theta = 1/1$; Refinemet method: Full-matrix least-squares on F^2.

displacement parameters are listed in Table 2. The intramolecular bond distances are given in Table 3. In Table 4 the significant dihedral angles are compared. The hydrogen coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations have been deposited at the Cambridge Crystallographic Data Centre. The CCDC numbers are 158432, 158433 and 158434, respectively, for N-chloro-N-(2,4,5-trichlorophenyl)-2-chloroacetamide (NC245TCPCA), N-(2,4,5-trichlorophenyl)-2-chloroacetamide (N245TCPCA) and N-(2,4,5-trichlorophenyl)-2,2,2-trichloroacetamide (N245TCPTCA). In Figs. 1, 2 and 3 we show the molecules of the title compounds as they appear in suitable projection with the numbering of the atoms used throughout the paper. In Fig. 4, typical hydrogen bridges in N245TCPCA are shown.

The compound N245TCPTCA shows two molecules in its asymmetric unit, while the other two compounds show one molecule each in their asymmetric units. First we shall discuss the intramolecular geometry of the title compounds. The individual data are given in Table 3. Comparing the C(i)-C(j) bond distances within the benzene rings of the three compounds, we find the following mean distances in Ångstrøm units. The observed minimum and maximum bond lengths in Å are given in parentheses: 1.387(1.375,1.402), 1.384(1.377,1.390) and 1.381(1.361,1.408) for the compounds N245TCPCA, NC245TCPCA and N245TCPTCA, respectively. The values given for the latter compound are the average of the two mean distances. The values for the two molecular units of N245TCPTCA are 1.382(1.361,1.408) and 1.379(1.364,1.397) Å, respectively. As may be

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \cdot 10^3$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
2,4,5-$Cl_3C_6H_2$·NHCO·CH_2Cl (N245TCPCA):				
Cl(1)	11355(3)	−620(1)	2417(2)	66(1)
C(2)	13500(8)	−155(1)	2219(6)	52(1)
C(3)	12171(7)	292(1)	2540(5)	42(1)
O(4)	9617(6)	321(1)	2601(5)	65(1)
N(5)	13972(6)	643(1)	2679(4)	43(1)
C(6)	13186(7)	1098(1)	2872(4)	39(1)
C(7)	11880(7)	1217(1)	4187(5)	40(1)
C(8)	11143(7)	1660(1)	4385(4)	40(1)
C(9)	11744(8)	1996(1)	3266(5)	43(1)
C(10)	13062(8)	1882(1)	1971(4)	44(1)
C(11)	13748(7)	1434(1)	1762(4)	41(1)
Cl(12)	9484(2)	1795(1)	6005(1)	50(1)
Cl(13)	10917(3)	2555(1)	3516(1)	63(1)
Cl(14)	15357(2)	1296(1)	118(1)	50(1)
2,4,5-$Cl_3C_6H_2$·NClCO·CH_2Cl (NC245TCPCA):				
Cl(1)	10716(1)	6516(1)	3609(1)	59(1)
C(2)	9858(1)	5773(2)	2388(3)	41(1)
C(3)	9038(1)	6198(2)	3210(3)	37(1)
O(4)	8974(1)	6895(2)	4576(2)	53(1)
N(5)	8336(1)	5714(2)	2302(2)	36(1)
Cl(6)	8415(1)	4813(1)	294(1)	41(1)
C(7)	7517(1)	6191(2)	2717(3)	33(1)
C(8)	6901(1)	5232(2)	3206(3)	38(1)
C(9)	6104(1)	5699(2)	3582(3)	40(1)
C(10)	5931(1)	7134(2)	3543(3)	37(1)
C(11)	6546(1)	8106(2)	3085(3)	36(1)
C(12)	7331(1)	7626(2)	2625(3)	34(1)
Cl(13)	7127(1)	3444(1)	3412(1)	60(1)
Cl(14)	4942(1)	7694(1)	4102(1)	54(1)
Cl(15)	6340(1)	9904(1)	3076(1)	51(1)
2,4,5-$Cl_3C_6H_2$·NHCO·CCl_3 (N245TCPTCA):				
Cl(1)	10000	13670(1)	3412(1)	57(1)
Cl(2)	12072(2)	13624(1)	5009(1)	57(1)
C(3)	10000	13113(5)	4460(4)	39(1)
C(4)	10000	11755(5)	4440(4)	37(1)
O(5)	10000	11235(4)	3774(3)	71(2)
N(6)	10000	11265(4)	5225(3)	43(1)
C(7)	10000	10071(5)	5441(4)	40(1)
C(8)	10000	9751(5)	6304(4)	38(1)
C(9)	10000	8593(4)	6560(3)	38(1)
C(10)	10000	7724(5)	5944(4)	38(1)
C(11)	10000	8019(5)	5082(4)	42(1)
C(12)	10000	9163(5)	4825(4)	41(1)
Cl(13)	10000	10836(1)	7086(1)	62(1)
Cl(14)	10000	6262(1)	6261(1)	53(1)
Cl(15)	10000	6934(2)	4310(1)	71(1)
Cl(16)	5000	4589(2)	8571(1)	67(1)
Cl(17)	7045(5)	3324(3)	7317(1)	173(2)
C(18)	5000	4162(6)	7488(4)	57(2)
C(19)	5000	5175(5)	6820(4)	36(1)
O(20)	5000	4930(4)	6075(3)	52(1)
N(21)	5000	6253(4)	7166(3)	42(1)
C(22)	5000	7334(5)	6724(4)	37(1)
C(23)	5000	8363(5)	7215(4)	43(1)
C(24)	5000	9444(5)	6835(4)	48(1)
C(25)	5000	9537(5)	5948(4)	45(1)
C(26)	5000	8533(6)	5465(4)	45(1)
C(27)	5000	7431(6)	5835(4)	43(1)
Cl(28)	5000	8274(2)	8326(1)	61(1)
Cl(29)	5000	10926(2)	5496(1)	66(1)
Cl(30)	5000	8627(2)	4354(1)	63(1)

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

Connection	Bond length	Connection	Bond length
N245TCPCA:		NC245TCPCA:	
Cl(1)-C(2)	1.742(4)	Cl(1)-C(2)	1.762(2)
C(2)-C(3)	1.515(5)	C(2)-C(3)	1.510(3)
C(3)-O(4)	1.227(4)	C(3)-O(4)	1.205(3)
C(3)-N(5)	1.324(4)	C(3)-N(5)	1.366(3)
N(5)-C(6)	1.416(4)	C(7)-N(5)	1.423(2)
C(6)-C(11)	1.390(5)	C(7)-C(12)	1.382(3)
C(6)-C(7)	1.391(4)	C(7)-C(8)	1.388(3)
C(7)-C(8)	1.375(5)	C(8)-C(9)	1.382(3)
C(8)-C(9)	1.402(5)	C(9)-C(10)	1.377(3)
C(7)-Cl(12)	1.721(3)	C(8)-Cl(13)	1.724(2)
C(9)-C(10)	1.378(5)	C(10)-C(11)	1.390(3)
C(9)-Cl(13)	1.720(3)	C(10)-Cl(14)	1.724(2)
C(10)-C(11)	1.384(5)	C(11)-C(12)	1.383(3)
C(11)-Cl(14)	1.724(3)	C(12)-Cl(15)	1.721(2)
N(5)-H(5N)	0.73(5)	N(5)-Cl(6)	1.709(2)
N245TCPTCA:		N245TCPTCA:	
Cl(1)-C(3)	1.748(6)	Cl(16)-C(18)	1.753(7)
Cl(2)-C(3)	1.771(4)	Cl(17)-C(18)	1.731(4)
C(3)-C(4)	1.544(8)	C(18)-C(19)	1.551(8)
C(3)-Cl(2)#1	1.771(4)	C(18)-Cl(17)#2	1.731(4)
C(4)-O(5)	1.193(7)	C(19)-O(20)	1.193(7)
C(4)-N(6)	1.343(7)	C(19)-N(21)	1.337(7)
N(6)-C(7)	1.398(7)	N(21)-C(22)	1.409(7)
N(6)-H(6)	0.8600	N(21)-H(21)	0.8600
C(7)-C(8)	1.390(8)	C(22)-C(27)	1.387(8)
C(7)-C(12)	1.408(8)	C(22)-C(23)	1.397(8)
C(8)-C(9)	1.376(8)	C(23)-C(24)	1.364(9)
C(8)-Cl(13)	1.733(6)	C(23)-Cl(28)	1.732(6)
C(9)-C(10)	1.376(8)	C(24)-C(25)	1.383(9)
C(10)-C(11)	1.383(8)	C(25)-C(26)	1.366(9)
C(10)-Cl(14)	1.733(6)	C(25)-Cl(29)	1.729(6)
C(11)-C(12)	1.361(8)	C(26)-C(27)	1.379(9)
C(11)-Cl(15)	1.722(5)	C(26)-Cl(30)	1.731(6)

seen, both the N-chlorination of N245TCPCA to give NC245TCPCA and replacement of two hydrogen atoms in the side chain to give N245TCPTCA slightly decrease the mean ring distances. In the first conversion, the crystal system remains the same, while the second conversion changes the crystal system from monoclinic to orthorhombic, the space group being changed in both the N-chlorination and side chain changes of N245TCPCA. Further, as may be seen, the conversion of N245TCPCA into NC245TCPCA

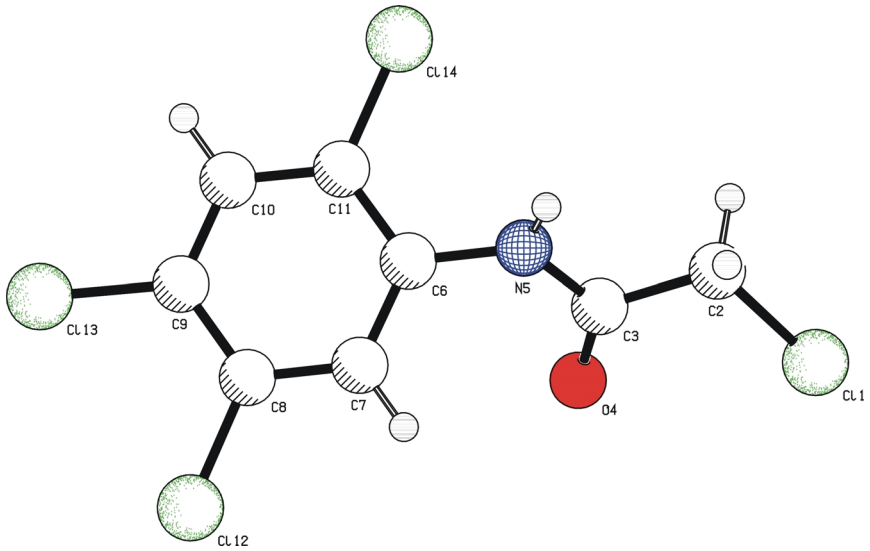

Fig. 1. Molecular geometry of N-(2,4,5-trichlorophenyl)-2-chloroacetamide, 2,4,5-$Cl_3C_6H_2$ · NHCO · CH_2Cl (N245TCPCA), with the numbering of atoms.

Table 4. Comparison of significant Dihedral angles (degree) (standard deviations).

Connection	Angle			
			N245TCPTCA	
	N245TCPCA	NC245TCPCA	Molecule 1	Molecule 2
Cl(1)-C(s)-C(o)-O	−12.2(5)	−3.4(3)	0.0	180.0
Cl(2)-C(s)-C(o)-O	–	–	−120.3(2)	59.5(3)
Cl(2)#-C(s)-C(o)-O	–	–	120.3(2)	−59.5(3)
Cl(1)-C(s)-C(o)-N	170.0(3)	177.4(2)	180.0	0.0
Cl(2)-C(s)-C(o)-N	–	–	59.7(3)	−120.5(3)
Cl(2)#-C(s)-C(o)-N	–	–	−59.7(3)	120.5(3)
C(s)-C(o)-N-C(1r)	176.1(3)	−170.1(2)	180.0	180.0
C(o)-N-C(1r)-C(2r)	50.1(5)	−122.7(2)	180.0	180.0
C(o)-N-C(1r)-C(6r)	−130.8(4)	57.6(3)	0.0	0.0
O-C(o)-N-C(1r)	−1.6(6)	10.8(3)	0.0	0.0

by N-chlorination slightly increased the C(ring)-N distance and the changes in the side chain to give N245TCPTCA has the opposite trend: 1.416(N245TCPCA), 1.423(NC245TCPCA) and, 1.398 (molecule 1) and 1.409 (molecule 2) (N245TCPTCA). The N-C(O) bond length increases in both cases, the change being more pronounced with N-chlorination. The C-O bond length decreases in both cases. The C(O)-C(side chain) length is affected only by the side chain changes.

As regards the bond angles, the ring angles are observed between 119.1° and 120.8° (N245TCPCA), 119.6° and 120.5° (NC245TCPCA) and, 117.7° and 122.0° (molecule 1), 118.5° and 121.9° (molecule 2) (N245TCPTCA). C2(ring)-C1(ring)-N and C6(ring)-C1(ring)-N angles for the compounds are 120.6° and 120.3° (N245TCPCA), 120.8° and 119.6° (NC245TCPCA) and, 119.1° and 123.2° (molecule 1), 117.7° and 123.8° (molecule 2) (N245TCPTCA). Similarly, the C2(ring)-C1(ring)-C6(ring) bond angles are 119.1° (N245TCPCA), 119.6° (NC245TCPCA) and, 117.7° (molecule 1) and 118.5° (molecule 2) (N245TCPTCA), while the C1(ring)-N-C(O) bond angles vary as 124.6° (N245TCPCA), 122.5° (NC245TCPCA) and 128.4°(molecule 1) and 127.1° (molecule 2) (N245TCPTCA). As may be seen, this angle is decreased by 2.1° on N-chlorination, while it is increased by a similar amount on replacement of H-atoms by Cl. But there are no significant changes in the N-C(O)-C(side chain) angles: 113.9° (N245TCPCA), 115.1° (NC245TCPCA) and, 113.3° (molecule 1) and 114.3° (molecule 2) (N245TCPTCA), while the N-C(O)-O bond angles change considerably, decrease by 3.8° on N-chlorination and increase with side chain changes: 124.0° (N245TCPCA), 120.2° (NC245TCPCA) and, 125.7° (molecule 1) and 127.2° (molecule 2) (N245TCPTCA).

The comparison of significant dihedral angles (Table 4) showed that there are changes in them on both N-chlorination and with side chain changes of N245TCPCA.

We have recently reported the crystal structure of several mono, di- and tri-substituted phenyl chloroacetamides [8, 9, 14, 15] and 2,2,2-trichloroacetamides [20]. We compare here the significant structural parameters of the present crystal structure of the compounds, N245TCPCA, NC245TCPCA and N245TCPTCA with those of other N-chlorophenyl chloroacetamides; N-phenyl acetamide, C_6H_5.NHCO.CH_3 (NPA) [17], N-phenyl-2,2,2-tri-

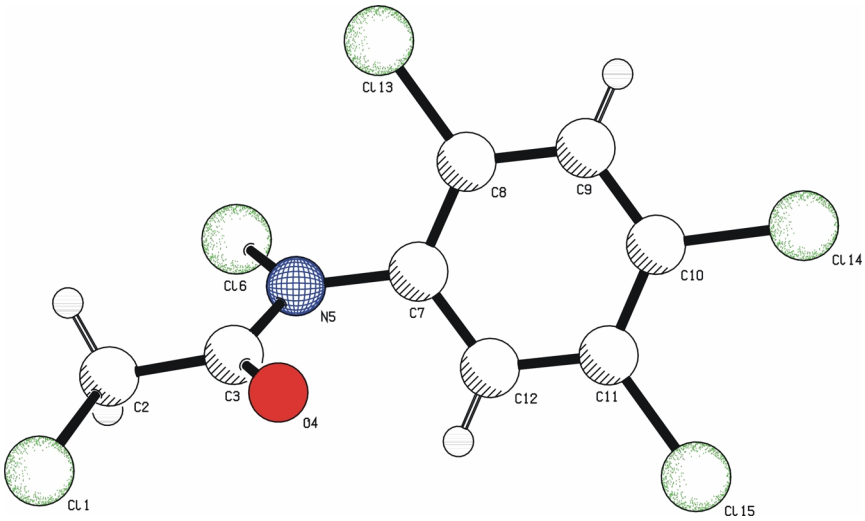

Fig. 2. Molecular geometry of N-chloro-(2,4,5-trichlorophenyl)-2-chloroacetamide, 2,4,5-$Cl_3C_6H_2$·NClCO·CH_2Cl (NC245TCPCA), with the numbering of atoms.

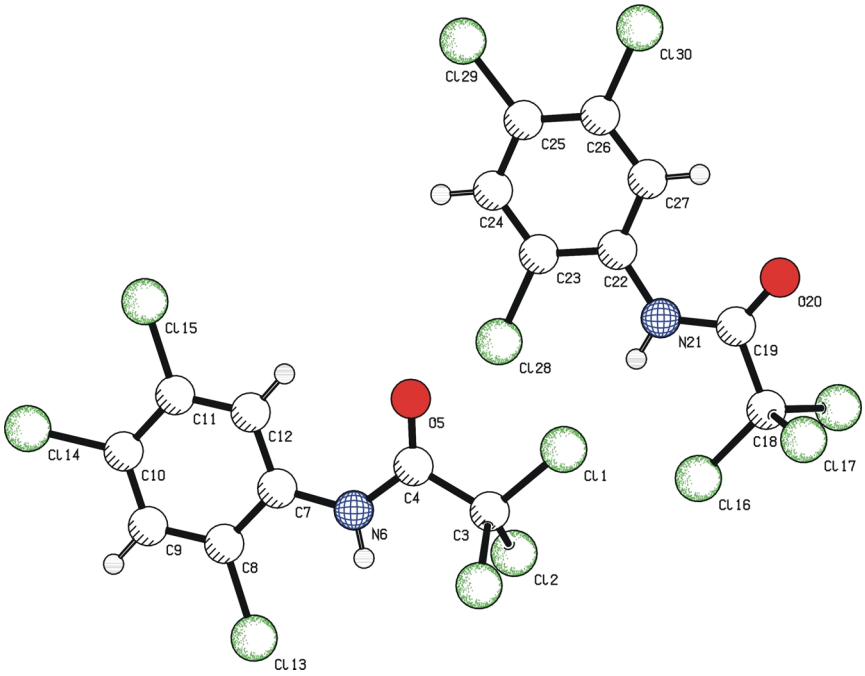

Fig. 3. Molecular geometry of N-(2,4,5-trichlorophenyl)-2,2,2-trichloroacetamide, 2,4,5-$Cl_3C_6H_2$·NHCO·CCl_3 (N245TCPCA), with the numbering of atoms.

chloroacetamide, C_6H_5.NHCO.CCl_3 (NPTCA) [8], N-(2-chlorophenyl)-2,2,2-trichloroacetamide, 2-ClC_6H_4.NHCO.CCl_3 (N2CPTCA), N-(4-chlorophenyl)-2,2,2-trichloroacetamide, 4-ClC_6H_4.NHCO.CCl_3 (N4CPTCA) [15], N-(2,4,6-trichlorophenyl)-2,2,2-trichloroacetamide, 2,4,6-$Cl_3C_6H_2$.NHCO.CCl_3 (N246TCPTCA) and N-(2,4,6-trichlorophenyl)-2-chloroacetamide, 2,4,6-$Cl_3C_6H_2$.NHCO.CH_2Cl (N246TCPCA) [20]. The crystal systems, space groups, side chain bond parameters are summarised in Table 5.

The comparison of the bond parameters revealed that there are significant changes in them with substitution in both the ring and in the side chain of the amides and on N-chlorination. But to draw general conclusions, further substantive data are to be collected with varying substitutions. Our work in this direction is in progress.

Table 5. Comparison of Crystal structure data of N-(substituted phenyl)-chloroacetamides.

Parameter	NPA	NPTCA	N2CPTCA	N4CPTCA	N246TCPTCA	N245TCPTCA	N246TCPCA	N245TCPCA	NC245TCPCA
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	triclinic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	Pbca	P21c	$Pna2_1$	Pbca	P1	Pmc21	$Pna2_1$	P21/n	P21/c
Z	8	4	4	8	4	4	8	4	4
Bond lengths:									
C(ring)-N	1.426	1.424	1.420	1.416	1.432	1.404	1.410	1.416	1.423
N-C(O)	1.330	1.337	1.340	1.328	1.332	1.340	1.345	1.324	1.366
C-O	1.226	1.211	1.207	1.210	1.193	1.193	1.216	1.227	1.205
C(O)-C(side)	1.476	1.564	1.561	1.555	1.531	1.548	1.513	1.515	1.510
Bond angles:									
C(2r)-C(1r)-C(6r)	121.2	119.9	119.0	119.6	118.1	118.1	116.5	119.1	119.6
C(2r)-C(1r)-N	115.7	122.1	119.9	122.2	119.5	118.4	121.7	120.6	120.8
C(6r)-C(1r)-N	122.7	117.9	121.1	118.1	122.4	123.5	121.9	120.3	119.6
C(1r)-N-C(O)	129.3	125.4	122.4	125.6	119.9	127.8	123.0	124.6	122.5
N-C(O)-C(side)	117.7	114.8	114.1	114.4	116.0	113.8	113.9	113.9	115.1
N-C(O)-O	121.7	126.3	125.8	126.0	124.9	126.5	123.5	124.0	120.2
O-C(O)-C(side)	120.4	118.9	120.1	119.6	119.3	119.7	122.7	122.1	124.7

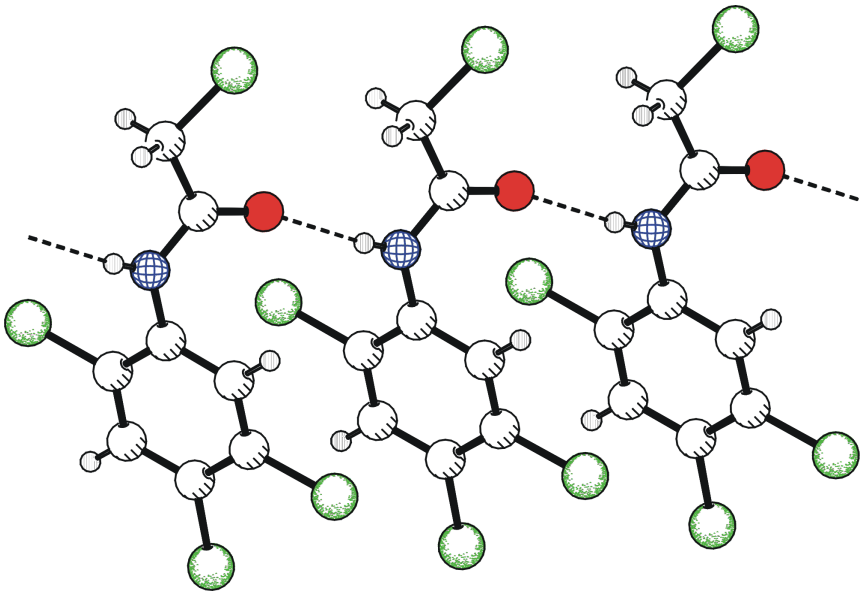

Fig. 4. Typical hydrogen bridges in N245TCPCA.

Acknowledgements

B. T. G. thanks the Alexander von Humboldt Foundation, Bonn, Germany for a resumption of research fellowship. Support of the Deutsche Forschungsgemeinschaft is also acknowledged.

[1] G. K. Semin, T. A. Babushkina, and G. G. Yakobson, Nuclear Quadrupole Resonance in Chemistry; Wiley, New York 1975.
[2] J. A. S. Smith (Ed.), Advances in Nuclear Quadrupole Resonances; Wiley, London 1974 – 83. Vols. 1 – 5.
[3] Al. Weiss and S. Wigand, Z. Naturforsch. **45a**, 195 (1990).
[4] Al. Weiss, Z. Naturforsch., **48a**, 477 (1993); Acta Cryst. **B51**, 523 (1995).
[5] The Chemistry of Amides, ed. J. Jabicky; Interscience, London 1970.
[6] R. Sandler and W. Karo, Organic Functional Group Preparations; Academic Press, London 1972, Vol. 3.
[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. **55a**, 721 (2000).
[13] D. K. Bhat and B. T. Gowda, J. Indian Chem. Soc. **77**, 279 (2000).
[14] S. Dou, H. Fuess, Al. Weiss, B. T. Gowda, and V. G. Krishnan, Z. Kristallogr. **212**, 532 (1997).
[15] B. T. Gowda, H. Paulus, and H. Fuess, Z. Naturforsch. **55a**, 711, 791 (2000); **56a**, 386 (2001).
[16] W. Pies, H. Rager, and Al. Weiss, Org. Mag. Reson. **3**, 147 (1971).
[17] C. J. Brown and D. E. C. Corbridge, Acta Cryst. **7**, 711 (1954); C. J. Brown, Acta Cryst. **21**, 442 (1966).
[18] S. C. Nyburg, J. K. Fawcett, and J. T. Szymanski, Acta. Cryst. **C43**, 2452 (1987).
[19] D. Groke, S. Dou, and Al. Weiss, Z. Naturforsch. **47a**, 160 (1992).
[20] B. T. Gowda, I. Svoboda, and H. Fuess, Z. Naturforsch. **55a**, 779 (2000).
[21] F. A. Berti and L. M. Ziti, Arch. Pharm. **285**, 372 (1952).
[22] G. M. Sheldrick: SHELXS-97. Program for the Solution of Crystal Structures, University of Göttingen, Germany 1990.
[23] G. M. Sheldrick: SHELXL-97. Program for Crystal Structure Determination, University of Göttingen, Germany 1997.
[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, Univesity 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).