Structural Studies on Substituted *N*-(phenyl)-2,2-Dichloroacetamides, 2/4-XC_6H_4·NHCO·$CHCl_2$ (X = H, Cl or CH_3)

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The effect of substitution in the phenyl ring on the crystal systems of amides of the type, 2/4-XC_6H_4-NHCO-$CHCl_2$ (X = H, Cl or CH_3), has been studied by determining the crystal structures of the compounds, *N*-(phenyl)-2,2-dichloroacetamide, C_6H_5-NHCO-$CHCl_2$ (PhDCA); *N*-(2-chlorophenyl)-2,2-dichloroacetamide, 2-ClC_6H_4-NHCO-$CHCl_2$ (*o*-ClPhDCA), *N*-(4-chlorophenyl)-2,2-dichloroacetamide, 4-ClC_6H_4-NHCO-$CHCl_2$ (*p*-ClPhDCA) and *N*-(4-methylphenyl)-2,2-dichloroacetamide, 4-$CH_3C_6H_4$-NHCO-$CHCl_2$ (*p*-CH_3PhDCA) and analysed the data along with our earlier crystal structures of the compounds, *N*-(phenyl)-2,2,2-trichloroacetamide (PhTCA), *N*-(2-chlorophenyl)-2,2,2-trichloroacetamide (*o*-ClPhTCA), *N*-(4-chlorophenyl)-2,2,2-trichloroacetamide (*p*-ClPhTCA), *N*-(4-methylphenyl)-2,2,2-trichloroacetamide (*p*-CH_3PhTCA); *N*-chloro-*N*-(phenyl)-2,2-dichloroacetamide (NClPhDCA), *N*-chloro-*N*-(phenyl)-2,2,2-trichloroacetamide (NClPhTCA) and *N*-(phenyl) acetamide (PhA). The crystal type, space group, formula units and lattice constants in Å of the new structures are; PhDCA: monoclinic, $P2_1/c$, $Z = 4$, $a = 8.785(3)$, $b = 11.139(4)$, $c = 9.521(3)$, $\beta = 97.47(2)°$; *o*-ClPhDCA: monoclinic, $P2_1/c$, $Z = 4$, $a = 4.711(2)$, $b = 11.234(6)$, $c = 19.191(8)$, $\beta = 98.12(2)°$; *p*-ClPhDCA: monoclinic, $P2_1/c$, $Z = 8$, $a = 18.627(5)$, $b = 11.533(3)$, $c = 9.583(3)$, $\beta = 102.43(2)°$, and *p*-CH_3PhDCA: orthorhombic, Pbca, $Z = 8$, $a = 9.464(3)$, $b = 9.894(3)$, $c = 21.973(7)$. The compound *p*-ClPhDCA shows two molecules in its asymmetric unit. This is in agreement with the multiple lines observed in the ^{35}Cl NQR spectra of the compound. The crystal systems of the chlorosubstituted and methyl substituted chloroacetamides get interchanged on replacement of the side chain -$CHCl_2$ by -CCl_3. C(i)-C(j) ring distances show no significant variations with the substitution either at the side chain or in the phenyl ring. C(ring)-N and C(O)-N bond distances are also not much affected by either ring or side chain substitution, but are affected by *N*-chlorination, while the C-O bond length is slightly shortened by the replacement of the -CH_3 group by -CCl_3, the introduction of electron withdrawing group into the phenyl ring or by *N*-chlorination. Deviations of C2(ring)-C1(ring)-N, C6(ring)-C1(ring)-N and C(ring)-N-C(O) bond angles from 120° narrow down on substitution either in the phenyl ring or in the side chain, but the latter increases on *N*-chlorination of the compounds.

Key words: Crystal Structures; Substituted *N*-phenyldichloroacetamides.

Introduction

The combined application of nuclear quadrupole resonance (NQR) spectroscopy and crystal structure studies has been extensively used to investigate the structural aspects of a variety of compounds including amides [1 - 3]. We are interested in the structural studies of amides in their crystalline state using both methods [4 - 10]. The amide moiety is a constituent of many biologically important compounds [11, 12]. Conjugation between nitrogen lone pair electrons and the carbonyl π-bond results in various physical and chemical properties [11]. Thus amides are essential for future development in such areas as polypeptide and protein chemistry [12]. Many amides exhibit fungicidal, herbicidal and pharmacological activities.

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Pies et al [13] have studied the ^{35}Cl NQR spectra of a number of *N* - (chlorophenyl) chloroacetamides. We have recently prepared several substituted amides of the configuration: $X_yC_6H_{5-y}$-$NHCO\text{-}CH_{3-y}$ Cl_y (where X = CH_3, NO_2 or Br and y = 1, 2 or 3) and measured their ^{35}Cl NQR and IR spectra [7 - 9, 14]. 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 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 spectrum. 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 [4].

There are no structural studies of many of these compounds to see how the -NHCO- bond parameters in $X_yC_6H_{5-y}$-$NHCO\text{-}CH_{3-y}Cl_y$ (where X = CH_3, NO_2, Cl or Br and y = 1, 2 or 3) vary with the substitution at different positions in the phenyl ring and in the side chain. Hence we investigated the crystal structure of several of these compounds. As a part of our efforts, we report in the present paper our results on the crystal structure of *N*-(phenyl)-2,2-dichloroacetamide, C_6H_5-NHCO-$CHCl_2$ (PhDCA), *N*-(2-chlorophenyl)-2,2-dichloroacetamide, 2-ClC_6H_4-NHCO-$CHCl_2$ (*o*-ClPhDCA), *N*-(4-chlorophenyl)-2,2-dichloroacetamide, 4-ClC_6H_4-NHCO-$CHCl_2$ (*p*-ClPhDCA) and *N*-(4-methylphenyl)-2,2-dichloroacetamide, 4-$CH_3C_6H_4$-NHCO-$CHCl_2$ (*p*-CH_3PhDCA). Further, the present data have been compared with the crystal structure of *N*-(phenyl)-2,2,2-trichloroacetamide, C_6H_5-NHCO-CCl_3 (PhTCA) [5], *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) [15], *N*-(4-methylphenyl)-2,2,2-trichloroacetamide, 4-$CH_3C_6H_4$-NHCO-CCl_3 (*p*-CH_3PhTCA) [10], *N*-chloro-*N*-(phenyl)-2,2-dichloroacetamide, C_6H_5-NClCO-$CHCl_2$ (NClPhDCA) [5], *N*-chloro-*N*-(phenyl)-2,2,2-trichloroacetamide, C_6H_5-NClCO-CCl_3 (NClPhTCA) [5] and *N*-(phenyl) acetamide, C_6H_5-NHCO-CH_3 (PhA) [16].

Experimental

Preparation and Characterisation of the Compounds

The compounds, PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, *p*-CH_3PhDCA were prepared from the corresponding anilines, dichloroacetic acid and phosphoryl chloride (Aldrich, Germany) [4, 13]. The commercial anilines were purified by zone refining. The liquids were purified by double distillations. Pure samples of the respective anilines were treated with mixtures of dichloroacetic acid (Aldrich, Germany) and phosphoryl chloride under constant stirring. The resulting mixtures were slowly warmed to expel HCl. Excess of phosphoryl chloride was hydrolysed by adding cold water dropwise under ice cold conditions. HCl produced was removed by treating with 2 M NaOH. 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 was checked by elemental analysis (C, H and N) and by determining their melting points. The compounds, PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, and *p*-CH_3PhDCA were further characterised by recording their infrared and ^{35}Cl NQR spectra and comparing the frequencies with literature values. All other reagents employed in the preparations and purification of the amides were of analytical grade.

X-ray Diffraction Studies

Small good crystals of PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, *p*-CH_3PhDCA were selected for X-ray diffraction and studied at room temperature. The collected intensity data were corrected for Lorentz

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of C_6H_5-NHCO-$CHCl_2$ (PhDCA); 2-ClC_6H_4-NHCO-$CHCl_2$ (*o*-ClPhDCA); 4-ClC_6H_4-NHCO-$CHCl_2$ (*p*-ClPhDCA) and 4-$CH_3C_6H_4$-NHCO-$CHCl_2$ (*p*-CH_3PhDCA). Diffractometer: Stoe-Stadi 4; Monochromator: Graphite (002); scan 2 θ/ω = 1 / 1; Refinement method: Full-matrix least-squares on F^2.

Compound	PhDCA	*o*-ClPhDCA	*p*-ClPhDCA	*o*-CH_3PhDCA
Chemical formula	$C_8H_7Cl_2NO$	$C_8H_6Cl_3NO$	$C_8H_6Cl_3NO$	$C_9H_9Cl_2NO$
Formula weight	204.05	238.49	238.49	218.07
Temperature, K	298(2)	299(2)	297(2)	298(2)
Wavelength, pm	71.073	71.069	71.073	71.069
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	Pbca
a, Å	8.785(3)	4.711(2)	18.627(5)	9.464(3)
b, Å	11.139(4)	11.234(6)	11.533(3)	9.894(3)
c, Å	9.521(3)	19.191(8)	9.583(3)	21.973(7)
β, deg.	97.47(2)	98.12(2)	102.43(2)	90
Volume, Å^3	923.8(5)	1005.5(8)	2010.4(10)	2057.5(11)
Z	4	4	8	8
D_{calcd}, g cm^{-3}	1.467	1.575	1.576	1.408
Abs. coeff., cm^{-1}	6.51	8.68	8.68	5.90
F(000)	416	480	960	896
Crystal size, mm^3	0.72 × 0.64 × 0.33	2.10 × 0.12 × 0.07	1.35 × 0.38 × 0.23	2.10 × 0.52 × 0.07
θ range, deg.	2.34 to 27.50	2.11 to 22.52	2.9 to 27.49	1.85 to 24.99
Index ranges	$-11 \le h \le 11$, $-14 \le k \le 14$, $0 \le l \le 12$	$0 \le h \le 5$, $-12 \le k \le 8$, $-20 \le l \le 20$	$-24 \le h \le 23$, $-14 \le k \le 2$, $0 \le l \le 12$	$0 \le h \le 11$, $-11 \le k \le 2$, $0 \le l \le 26$
Reflections coll.	4374	3071	5670	2204
Independent refl.	2121	1306	4587	1809
[*R*(int)]	0.0162	0.0240	0.0290	0.0082
Absorption corr.	numerical	Psi-scan	numerical	numerical
Max. and min. transm.	0.823 and 0.674	0.935 and 0.882	0.852 and 0.749	0.958 and 0.744
Data	2121	1306	4584	1803
Restraints/parameters	0/113	0/122	0/242	0/124
Goodness-of-fit on F^2	1.072	1.071	1.078	1.082
Final *R* [$I > 2\sigma(I)$]	*R*1 = 0.0360, *wR*2 = 0.0943	*R*1 = 0.0289, *wR*2 = 0.0686	*R*1 = 0.0625, *wR*2 = 0.1652	*R*1 = 0.0368, *wR*2 = 0.0890
R indices (all data)	*R*1 = 0.0408, *wR*2 = 0.0995	*R*1 = 0.0456, *wR*2 = 0.0779	*R*1 = 0.0910, *wR*2 = 0.2011	*R*1 = 0.0437, *wR*2 = 0.1010
Extinction coeff.	0.022(2)	0.0051(13)	0.018(2)	0.0030(6)
Largest diff. Peak and hole e$^-$ Å^3	0.318 and –0.392	0.168 and –0.192	0.434 and –0.448	0.430 and –0.337

polarisation and absorption. The positional parameters were determined by direct methods and least squares refinement (SHELXL-93) [17 - 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, to 0.97 Å for the CH_2Cl group and to 0.98 Å for the $CHCl_2$ group. Further experimental conditions for structure determinations and refinements are given in Table 1.

Results and Discussion

The crystallographic data for the compounds, PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, *p*-CH_3PhDCA are shown 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. Further information on the crystal structure determinations has been deposited at the Cambridge Crystallographic Data Centre (CCDC). The CCDC numbers are 147543, 147544, 147545 and 147546 for *N*-(phenyl)-2,2-dichloroacetamide, *N*-(2-chlorophenyl)-2,2-dichloroacetamide, *N*-(4-chlorophenyl)-2,2-dichloroacetamide, and *N*-(4-methylphenyl)-2,2-dichloroacetamide, respectively.

Figures 1, 3, 5, and 7 show the molecules of PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, *p*-CH_3PhDCA as they appear in suitable projection and with the num-

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)
C_6H_5-NHCO-$CHCl_2$ (PhDCA):				
Cl(1)	1888(1)	379(1)	577(1)	68(1)
Cl(2)	5076(1)	778(1)	1731(1)	66(1)
C(3)	3468(2)	1369(2)	647(2)	43(1)
C(4)	3004(2)	2563(2)	1258(2)	44(1)
O(5)	2841(2)	2656(1)	2513(1)	66(1)
N(6)	2799(2)	3446(1)	302(1)	43(1)
C(7)	2336(2)	4648(1)	541(2)	43(1)
C(8)	1400(2)	4936(2)	1565(2)	48(1)
C(9)	957(2)	6117(2)	1711(2)	61(1)
C(10)	1414(3)	7000(2)	857(3)	70(1)
C(11)	2340(3)	6716(2)	–159(3)	71(1)
C(12)	2807(2)	5544(2)	–325(2)	57(1)
2-ClC_6H_4-NHCO-$CHCl_2$ (*o*-ClPhDCA):				
Cl(1)	2649(2)	1219(1)	5368(1)	71(1)
Cl(2)	3999(2)	3473(1)	4768(1)	77(1)
C(3)	3943(6)	1905(3)	4660(1)	41(1)
C(4)	2026(6)	1635(3)	3969(1)	41(1)
O(5)	–562(4)	1663(3)	3935(1)	73(1)
N(6)	3448(5)	1421(2)	3429(1)	37(1)
C(7)	2145(5)	1236(2)	2725(1)	35(1)
C(8)	3051(5)	319(3)	2332(2)	39(1)
C(9)	1862(7)	154(3)	1636(2)	53(1)
C(10)	–230(7)	914(3)	1335(2)	61(1)
C(11)	–1169(7)	1830(3)	1720(2)	55(1)
C(12)	9(6)	1992(3)	2411(2)	44(1)
Cl(13)	5691(2)	–652(1)	2708(1)	57(1)

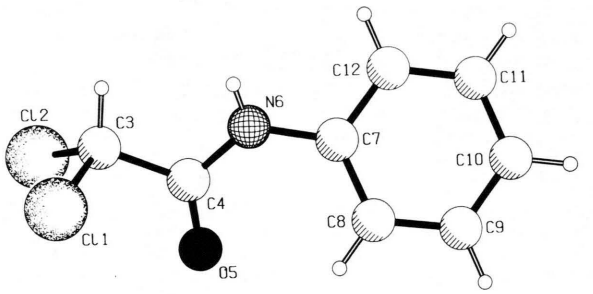

Fig. 1. Molecular geometry of *N*-(phenyl)-2,2-dichloroacetamide, C_6H_5-NHCO-$CHCl_2$ (PhDCA), with the numbering of atoms.

bering of the atoms used throughout the paper. The Figs 2, 4, 6 and 8 project the unit cells of the compounds, PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, and *p*-CH_3PhDCA.

p-ClPhDCA shows two molecules in its asymmetric unit. This agrees with the 6 frequencies observed in the ^{35}Cl NQR spectra [13]. The phenyl-, *N*-chloro-phenyl-, 2-chlorophenyl- and 4-chlorophenyl- dichloroacetamides crystallise in monoclinic symmetry, while 4-methylphenyl dichloroacetamide crystallises in orthorhombic symmetry. Contrary to this, 2-chlorophenyl and 4-chlorophenyl trichloroacetamides crystallise in orthorhombic symmetry, while the 4-methylphenyl trichloroacetamide crystallises in the monoclinic symmetry. The crystal symmetries of the chlorosubstituted and methyl substituted chloroacetamides are interchanged on replacement of the side chain -$CHCl_2$ by -CCl_3. The parent compound *N*-phenyl acetamide crystallises in the or-

Table 2 (continued).

Atom	x	y	z	U(eq)
4-ClC_6H_4-NHCO-$CHCl_2$ (*p*-ClPhDCA):				
Cl(1)	301(1)	4470(1)	1902(1)	86(1)
Cl(2)	–608(1)	2651(2)	369(2)	126(1)
C(3)	277(2)	3242(4)	811(4)	62(1)
C(4)	800(2)	2307(3)	1581(4)	55(1)
O(5)	948(2)	2206(2)	2874(3)	72(1)
N(6)	1049(2)	1616(3)	665(3)	54(1)
C(7)	1476(2)	602(3)	972(3)	51(1)
C(8)	1800(2)	158(3)	–89(4)	59(1)
C(9)	2191(2)	–863(4)	106(4)	63(1)
C(10)	2263(2)	–1440(3)	1372(4)	62(1)
C(11)	1956(2)	–1015(4)	2450(4)	65(1)
C(12)	1562(2)	–3(3)	2260(4)	59(1)
Cl(13)	2745(1)	–2745(1)	1609(2)	92(1)
Cl(14)	2148(1)	4225(1)	1071(1)	70(1)
Cl(15)	3556(1)	4635(1)	336(1)	71(1)
C(16)	2821(2)	3642(3)	239(4)	56(1)
C(17)	3128(2)	2503(3)	970(3)	52(1)
O(18)	3147(2)	2329(2)	2231(3)	67(1)
N(19)	3374(2)	1790(3)	91(3)	56(1)
C(20)	3734(2)	719(3)	398(3)	51(1)
C(21)	3892(2)	97(3)	–742(4)	57(1)
C(22)	4233(2)	–954(4)	–543(4)	63(1)
C(23)	4436(2)	–1412(3)	814(4)	62(1)
C(24)	4291(2)	–810(4)	1967(4)	65(1)
C(25)	3946(2)	254(3)	1771(4)	59(1)
Cl(26)	4873(1)	–2748(1)	1084(2)	91(1)
4-$CH_3C_6H_4$-NHCO-$CHCl_2$ (*p*-CH_3PhDCA):				
Cl(1)	995(1)	2838(1)	6313(1)	75(1)
Cl(2)	1083(1)	239(1)	5713(1)	69(1)
C(3)	518(2)	1930(2)	5653(1)	44(1)
C(4)	1249(2)	2575(2)	5105(1)	40(1)
O(5)	2532(2)	2592(2)	5064(1)	58(1)
N(6)	368(2)	3091(2)	4696(1)	42(1)
C(7)	801(2)	3707(2)	4139(1)	40(1)
C(8)	91(3)	3384(3)	3612(1)	53(1)
C(9)	484(3)	3983(3)	3067(1)	63(1)
C(10)	1571(3)	4909(3)	3040(1)	60(1)
C(11)	2265(3)	5218(3)	3576(1)	63(1)
C(12)	1890(2)	4631(2)	4123(1)	52(1)
C(13)	1963(4)	5599(4)	2449(1)	95(1)

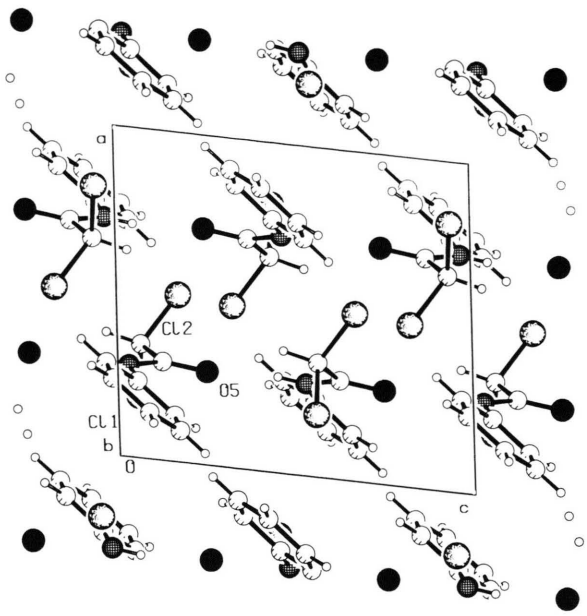

Fig. 2. Projection of the unit cell of PhDCA along [010].

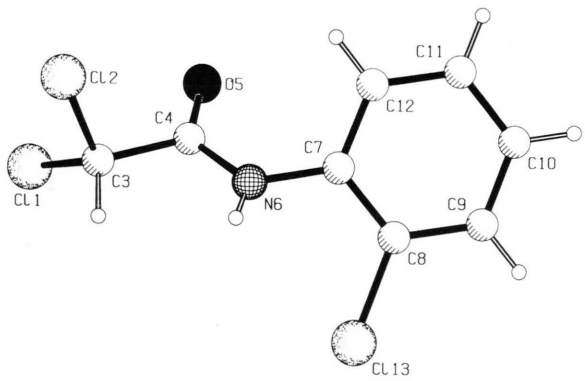

Fig. 3. Molecular geometry of *N*-(2-chlorophenyl)-2,2-dichloroacetamide, 2-ClC_6H_4-NHCO-$CHCl_2$ (*o*-ClPhDCA), with the numbering of atoms.

thorhombic symmetry. It may be difficult to generalise these aspects, unless extensive work is carried out with the change of both the substituent and the site of the substitution in the phenyl ring. Work in this direction is in progress in our group.

We shall now consider the intramolecular geometry of the four title compounds, PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, and *p*-CH_3PhDCA, in comparison with the componds PhTCA, *o*-ClPhTCA, *p*-ClPhTCA, *p*-CH_3PhTCA, NClPhDCA, NClPhTCA and PhA. We find that the range of C(i)-C(j) bond distances within

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

PhDCA:			
Cl(1)-C(3)	1.768(2)	Cl(2)-C(3)	1.764(2)
C(3)-C(4)	1.528(2)	C(4)-O(5)	1.226(2)
C(4)-N(6)	1.337(2)	N(6)-C(7)	1.425(2)
o-ClPhDCA:			
Cl(1)-C(3)	1.745(3)	Cl(2)-C(3)	1.773(3)
C(3)-C(4)	1.525(4)	C(4)-O(5)	1.212(3)
C(4)-N(6)	1.333(3)	N(6)-C(7)	1.418(3)
C(8)-Cl(13)	1.733(3)		
p-CH_3PhDCA:			
Cl(1)-C(3)	1.764(2)	Cl(2)-C(3)	1.761(2)
C(3)-C(4)	1.528(3)	C(4)-O(5)	1.218(2)
C(4)-N(6)	1.327(3)	N(6)-C(7)	1.427(3)
p-ClPhDCA:			
Cl(1)-C(3)	1.755(4)	Cl(2)-C(3)	1.750(4)
C(3)-C(4)	1.532(5)	C(4)-O(5)	1.216(4)
C(4)-N(6)	1.340(5)	N(6)-C(7)	1.410(5)
C(7)-Cl(12)	1.397(5)	C(10)-Cl(13)	1.743(4)
Cl(14)-C(16)	1.758(4)	Cl(15)-C(16)	1.772(4)
C(16)-C(17)	1.540(5)	C(17)-O(18)	1.218(4)
C(17)-N(19)	1.327(4)	N(19)-C(20)	1.406(5)

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

PhDCA:			
C(4)-C(3)-Cl(1)	108.08(12)	C(4)-C(3)-Cl(2)	109.56(11)
Cl(2)-C(3)-Cl(1)	110.77(9)	O(5)-C(4)-N(6)	125.4(2)
O(5)-C(4)-C(3)	121.0(2)	N(6)-C(4)-C(3)	113.62(13)
C(4)-N(6)-C(7)	126.77(13)	C(12)-C(7)-C(8)	119.9(2)
C(12)-C(7)-N(6)	117.8(2)	C(8)-C(7)-N(6)	122.3(2)
o-ClPhDCA:			
C(4)-C(3)-Cl(1)	111.1(2)	C(4)-C(3)-Cl(2)	107.2(2)
Cl(1)-C(3)-Cl(2)	110.4(2)	O(5)-C(4)-N(6)	125.0(3)
O(5)-C(4)-C(3)	120.7(2)	N(6)-C(4)-C(3)	114.3(2)
C(4)-N(6)-C(7)	124.7(2)	C(8)-C(7)-C(12)	118.7(3)
C(8)-C(7)-N(6)	120.3(2)	C(7)-C(8)-Cl(13)	120.1(2)
C(9)-C(8)-Cl(13)	119.1(2)		
p-CH_3PhDCA:			
C(4)-C(3)-Cl(1)	108.6(2)	C(4)-C(3)-Cl(2)	108.5(2)
Cl(2)-C(3)-Cl(1)	110.2(1)	O(5)-C(4)-N(6)	124.7(2)
O(5)-C(4)-C(3)	121.0(2)	N(6)-C(4)-C(3)	114.2(2)
C(4)-N(6)-C(7)	124.4(2)	C(12)-C(7)-N(6)	121.4(2)
C(8)-C(7)-N(6)	118.8(2)		
p-ClPhDCA:			
C(4)-C(3)-Cl(1)	110.4(3)	C(4)-C(3)-Cl(2)	108.1(3)
Cl(1)-C(3)-Cl(2)	111.1(2)	O(5)-C(4)-N(6)	125.2(4)
O(5)-C(4)-C(3)	122.6(3)	N(6)-C(4)-C(3)	112.1(3)
C(4)-N(6)-C(7)	128.1(3)	C(8)-C(7)-C(12)	118.6(4)
C(8)-C(7)-N(6)	118.0(3)	C(12)-C(7)-N(6)	123.4(3)
C(17)-C(16)-Cl(14)	110.6(2)	C(17)-C(16)-Cl(15)	108.7(3)
Cl(14)-C(16)-Cl(15)	110.3(2)	O(18)-C(17)-N(19)	126.0(4)
O(18)-C(17)-C(16)	121.4(3)	N(19)-C(17)-C(16)	112.6(3)
C(17)-N(19)-C(20)	128.7(3)	C(21)-C(20)-C(25)	118.5(3)
C(21)-C(20)-N(19)	117.4(3)	C(25)-C(20)-N(19)	124.1(3)

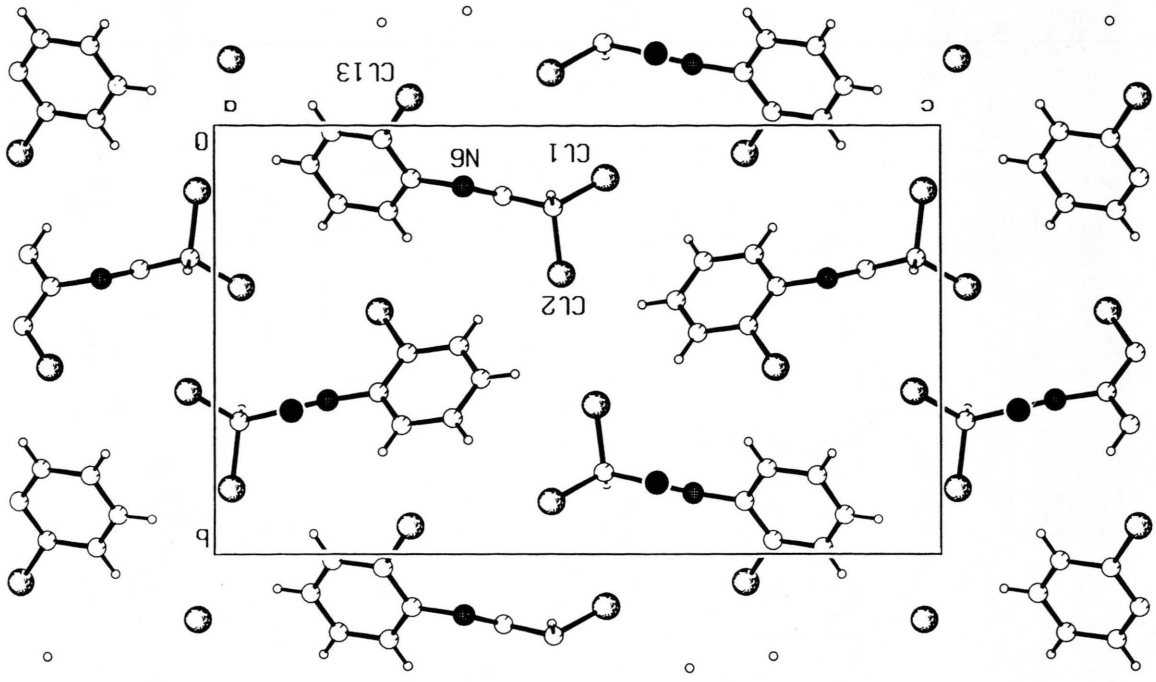

Fig. 4. Projection of the unit cell of *o*-ClPhDCA along [100].

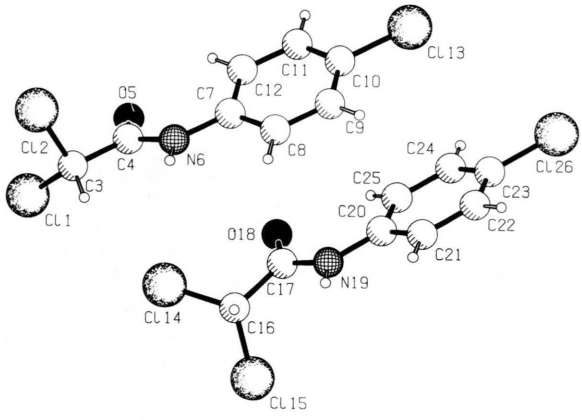

Fig. 5. Molecular geometry of *N*-(4-chlorophenyl)-2,2-dichloroacetamide, 4-ClC_6H_4-NHCO-$CHCl_2$ (*p*-ClPhDCA) with the numbering of atoms.

the phenyl rings of the compounds do not significantly vary with the substitution either at the side chain or in the phenyl ring. The mean distances of all the compounds lie in the range, 1.374 - 1.387 Å, the minimum mean value occuring in *N*-chloro-*N*-phenyl dichloroacetamide (NClPhDCA) and the maximum mean value in *N*-phenyl acetamide (PhA). Also the range of the six ring distances for the compound PhA is wider (1.366 - 1.413 Å); it narrows down on substitution either in the phenyl ring or at the side chain, the narrowest range being 1.378 - 1.386 Å for the *p*-CH_3PhDCA, with most of the ring distances of all the compounds being in the range of 1.370 - 1.390 Å. C(ring)-Cl distances of the compounds *o*-ClPhDCA and *p*-ClPhDCA are 1.733 Å and 1.743 Å, when compared to the distances of 1.737 Å and 1.740 Å for *o*-ClPhTCA and *p*-ClPhTCA. The C(ring)-N distances for the compounds, PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, *p*-CH_3PhDCA, PhTCA, *o*-ClPhTCA, *p*-ClPhTCA, *p*-CH_3PhTCA, NClPhDCA, NClPhTCA and PhA are 1.425, 1.418, 1.418, 1.427, 1.424, 1.420, 1.416, 1.427, 1.437, 1.443 and 1.426 Å, respectively. It is evident from these values that the C(ring)-N distance is not much affected by either ring or side chain substitution, but it is affected by *N*-chlorination. A similar trend is observed for the C(O)-N bond distance, while the C-O bond length is slightly shortened by the replacement of -CH_3 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), and 1.197 Å and 1.200 Å for the *N*-chloro-*N*-phenyl dichloroacetamide

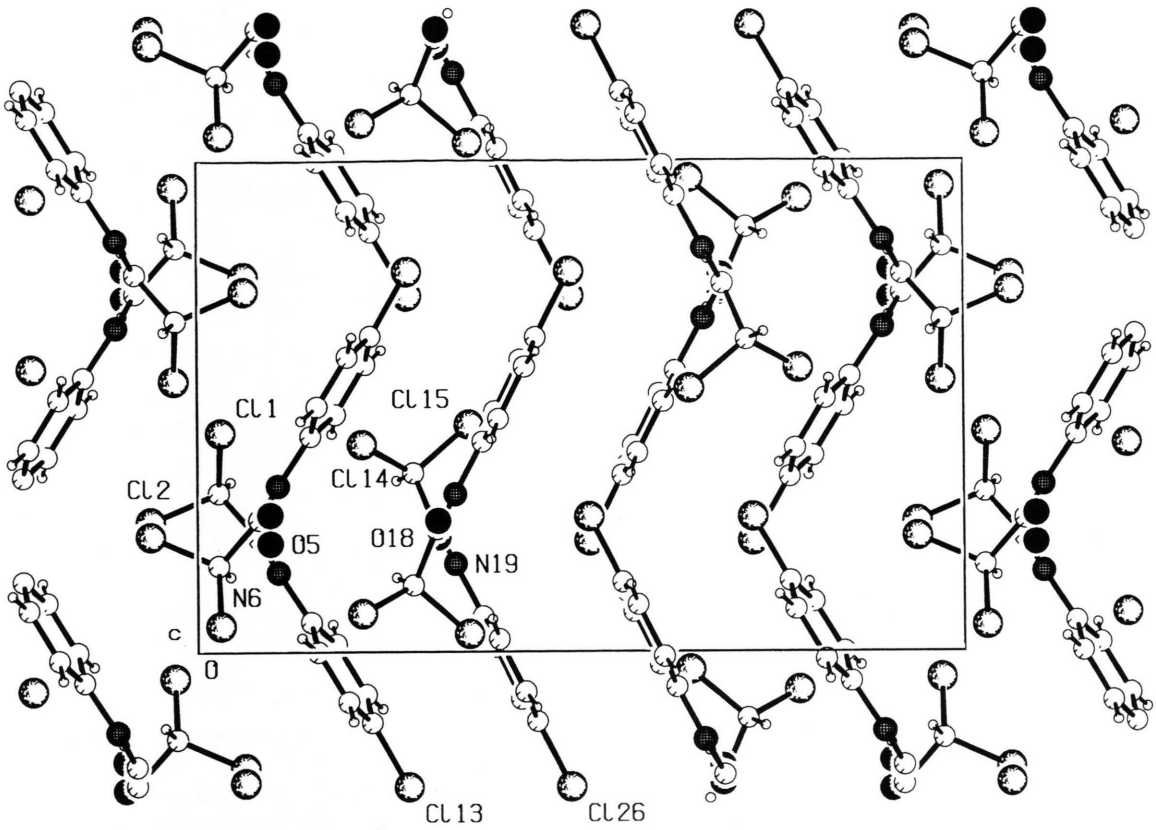

Fig. 6. Projection of the unit cell of *p*-ClPhDCA along [001].

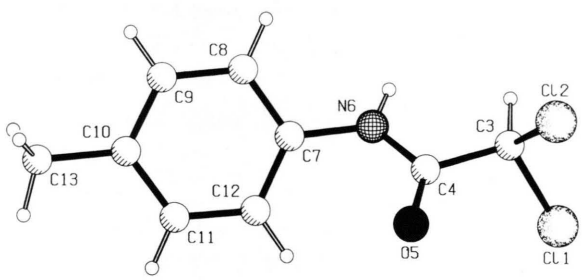

Fig. 7. Molecular geometry of N-(4-methylphenyl)-2,2-dichloroacetamide, 4-$CH_3C_6H_4$-NHCO-$CHCl_2$ (*p*-CH_3PhDCA) with the numbering of atoms.

and *N*-chloro-*N*-phenyl trichloroacetamide, respectively. The C(O)-C(side) bond lengths are 1.528, 1.525, 1.535, 1.528, 1.564, 1.561, 1.555, 1.550, 1.531, 1.562 and 1.476 Å for the compounds, PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, *p*-CH_3PhDCA, PhTCA, *o*-ClPhTCA, *p*-ClPhTCA, *p*-CH_3PhTCA, NClPhDCA, NClPhTCA and PhA, respectively. This distance increases only on substitution in the side chain. The mean C(side)-Cl bond lengths generally remain in the range of 1.759 - 1.768 Å.

As regards the bond angles, the ring angles are observed for the different compounds in the following ranges: 119.3 - 121.0° (PhDCA), 118.7 - 120.8° (*o*-ClPhDCA), 118.5 - 121.3° (*p*-ClPhDCA), 117.6 - 121.7° (*p*-CH_3PhDCA), 119.5 - 120.7 (PhTCA), 119.0 - 120.9° (*o*-ClPhTCA), 119.0 - 121.3° (*p*-ClPhTCA), 116.8 - 122.4°, (*p*-CH_3PhTCA), 118.1 - 121.2° (NClPhDCA), 118.6 - 121.5° (NClPhTCA), and 119.2 - 121.3° (PhA). The deviations of the individual values from 120° are relatively larger for the methyl substituted chloroacetamides and minimum for ring unsubstituted actamides, further narrowing with side chain substitution by Cl. The C2(ring)-C1(ring)-N and C6(ring)-C1(ring)-N angles for all the ten compounds are 117.8° and 122.3° (PhDCA), 120.3° and 121.0° (*o*-ClPhDCA), 117.4° and 124.1° (*p*-ClPhDCA), 118.8° and 121.4° (*p*-CH_3PhDCA),

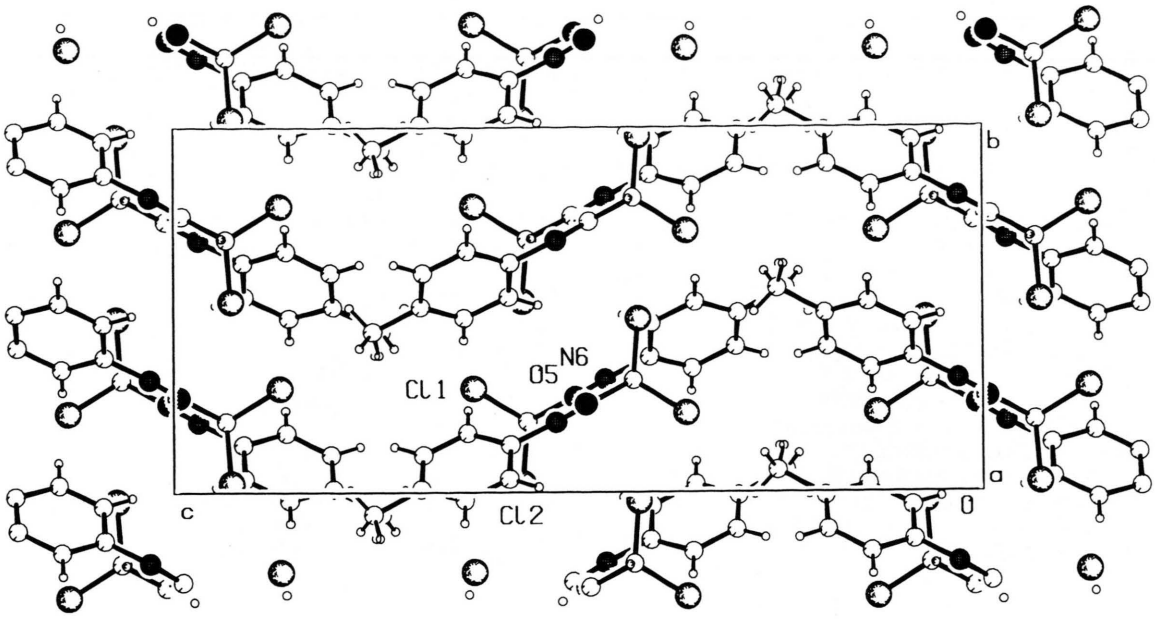

Fig. 8. Projection of the unit cell of *p*-CH_3PhDCA along [100] on to the *bc* plane.

117.9° and 122.1° (PhTCA), 119.9° and 121.1° (*o*-ClPhTCA), 118.1° and 122.2° (*p*-ClPhTCA), 117.6° and 123.4° (*p*-CH_3PhTCA), 118.4° and 120.3° (NClPhDCA), 118.8° and 119.6° (NClPhTCA) and 115.7° and 122.7° (PhA), respectively. Generally, deviations of these angles from 120° narrow down on substitution either in the phenyl ring or in the side chain, except for those compounds in which two molecules are found in their asymmetric units. Similarly the C2(ring)-C1(ring)-C6(ring) bond angles are 119.9°, 118.7°, 118.6°, 119.8°, 119.9°, 119.0°, 119.6° , 119.4°, 121.2, 121.5° and 121.2° for the compounds, PhDCA, *o*-ClPhDCA, *p*-ClPhDCA, *p*-CH_3PhDCA, PhTCA, *o*-ClPhTCA, *p*-ClPhTCA, *p*-CH_3PhTCA, NClPhDCA, NClPhTCA and PhA, respectively. Within these compounds, the C(ring)-N-C(O) bond angles vary as 126.8° (PhDCA), 124.7° (*o*-ClPhDCA), 128.4° (*p*-ClPhDCA), 124.4° (*p*-CH_3PhDCA), 125.4° (PhTCA), 122.4° (*o*-ClPhTCA), 125.6° (*p*-ClPhTCA), 124.1° (*p*-CH_3PhTCA), 129.2° (NClPhDCA), 132.3° (NClPhTCA) and 129.3° (PhA). This angle decreases either on side chain substitution of PhA by Cl or phenyl ring substitution, but increases on N-chlorination of the compounds. The N-C(O)-C(side chain) angles are 113.6° (PhDCA), 114.3° (*o*-ClPhDCA), 112.4° (*p*-ClPhDCA), 114.2° (*p*-CH_3PhDCA), 114.8° (PhTCA), 114.1° (*o*-ClPhTCA), 114.4° (*p*-ClPhTCA), 116.5° (*p*-CH_3PhTCA), 113.4° (NClPhDCA), 118.6° (NClPhTCA) and 117.7° (PhA). This angle gets stabilised around 114° except for the *N*-chloro compounds, and deviations by about 2° are observed for the compounds having 2 molecules in their asymmetric units. Similarly, the O-C(O)-C(side chain) angles are 121.0° (PhDCA), 120.7° (*o*-ClPhDCA), 122.0° (*p*-ClPhDCA), 121.0° (*p*-CH_3PhDCA), 118.9° (PhTCA), 120.1° (*o*-ClPhTCA), 119.6° (*p*-ClPhTCA), 118.2° (*p*-CH_3PhTCA), 122.5° (NClPhDCA), 118.3° (NClPhTCA) and 120.4° (PhA), while the O-C(O)-N angles are 125.4° (PhDCA), 125.0° (*o*-ClPhDCA), 125.6° (*p*-ClPhDCA), 124.7° (*p*-CH_3PhDCA), 126.3° (PhTCA), 125.8° (*o*-ClPhTCA), 126.0° (*p*-ClPhTCA), 125.3° (*p*-CH_3PhTCA), 124.1° (NClPhDCA), 123.0° (NClPhTCA) and 121.7° (PhA).

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