# Effect of Substitution on the Molecular Geometry of *N*-(2/3/4-Substituted-phenyl)-2,2-dichloro-acetamides, 2/3/4-$XC_6H_4NH$-CO-$CHCl_2$ (X = $CH_3$ or Cl)

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The effect of ring substitution on the molecular geometry of amides of the type 2/3/4-$XC_6H_4NH$-CO-$CHCl_2$ (X = $CH_3$ or Cl) has been studied by determining the crystal structures of the compounds *N*-(2-methylphenyl)-2,2-dichloro-acetamide, 2-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**2MPDCA**); *N*-(3-methylphenyl)-2,2-dichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**3MPDCA**) and *N*-(3-chlorophenyl)-2,2-dichloro-acetamide, 3-$ClC_6H_4NH$-CO-$CHCl_2$ (**3CPDCA**). The results are analyzed along with our earlier crystal structures of the amides *N*-(phenyl)-2,2-dichloro-acetamide, $C_6H_5NH$-CO-$CHCl_2$ (**PDCA**); *N*-chloro-*N*-(phenyl)-2,2-dichloro-acetamide, $C_6H_5NCl$-CO-$CHCl_2$ (**NCPDCA**); *N*-(4-methylphenyl)-2,2-dichloro-acetamide, 4-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**4MPDCA**); *N*-(2-chlorophenyl)-2,2-dichloro-acetamide, 2-$ClC_6H_4NH$-CO-$CHCl_2$ (**2CPDCA**); *N*-(4-chlorophenyl)-2,2-dichloro-acetamide, 4-$ClC_6H_4NH$-CO-$CHCl_2$ (**4CPDCA**). The results have also been compared and correlated with the crystal structure data of trichloro-acetamide analogues of the type 2/3/4-$XC_6H_4NH$-CO-$CCl_3$ (X = $CH_3$ or Cl): *N*-(phenyl)-2,2,2-trichloro-acetamide, *N*-(2-methylphenyl)-2,2,2-trichloro-acetamide, *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide, *N*-(4-methylphenyl)-2,2,2-trichloro-acetamide, *N*-(2-chlorophenyl)-2,2,2-trichloro-acetamide, *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide, *N*-(4-chlorophenyl)-2,2,2-trichloro-acetamide, *N*-chloro-*N*-(phenyl)-2,2,2-trichloro-acetamide and *N*-(phenyl)-acetamide. The crystal system, space group, formula units and lattice constants in Å of the new structures are: **2MPDCA**: monoclinic, $P2_1/n$, $Z = 4$, $a = 4.7059(5)$, $b = 11.600(1)$, $c = 18.918(2)$, $\beta = 94.702(9)^\circ$; **3MPDCA**: orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 4.759(1)$, $b = 10.543(3)$, $c = 20.205(5)$; **3CPDCA**: orthorhombic, *Pnma*, $Z = 4$, $a = 9.935(1)$, $b = 6.997(1)$, $c = 14.140(2)$. **2MPDCA**, **3MPDCA** and **3CPDCA** show a molecule each in their asymmetric units, in agreement with the observed $^{35}$Cl NQR spectra of the compounds.

*Key words:* Crystal Structures; *N*-(2/3/4-Substituted-phenyl)-2,2-dichloro-acetamides.

## 1. Introduction

The combined use of nuclear quadrupole resonance (NQR) spectroscopy and crystal structure studies has been valuable for investigating the structural aspects of a variety of compounds including amides [1, 2]. We have used these methods for the structural studies of amides in their crystalline state [3 – 18]. The amide moiety is an important constituent of many biologically significant compounds. Conjugation between nitrogen lone pair electrons and the carbonyl $\pi$-bond in it results in diverse physical and chemical properties [19]. Thus amides are of fundamental chemical interest and are central to future development in such areas as polypeptide and protein chemistry.

Pies et al. [20] have studied the $^{35}$Cl NQR spectra of a number of *N*-(chlorophenyl)chloro-acetamides. We have synthesized several substituted amides of the general formula: $X_yC_6H_{5-y}NH$-CO-$CH_{3-y}Cl_y$ (X = $CH_3$, $NO_2$ or Br and $y = 1$, 2 or 3) and measured their $^{35}$Cl NQR [3 – 8]. In the process we have noticed some interesting features. Some of the corresponding *N*-chloro compounds have also been prepared and their $^{35}$Cl(N) and $^{35}$Cl($\omega$) NQR measured [3, 4, 9]. To see how the -NHCO- bond parameters in $X_yC_6H_{5-y}NH$-CO-$CH_{3-y}Cl_y$ (X = $CH_3$, $NO_2$, Cl or Br and $y = 1$, 2 or 3) vary with substitution at different positions in the phenyl ring and in the side chain, we have undertaken detailed structural studies of this class of compounds [8 – 18]. As part of our efforts in this direction, we

Table 1. Experimental conditions for the crystal structure determination and crystallographic data of *N*-(2-methylphenyl)-2,2-dichloro-acetamide, 2-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**2MPDCA**); *N*-(3-methylphenyl)-2,2-dichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**3MPDCA**) and *N*-(3-chlorophenyl)-2,2-dichloro-acetamide, 3-$ClC_6H_4NH$-CO-$CHCl_2$ (**3CPDCA**). Diffractometer: Stoe-Stadi4; monochromator: graphite (002); scan $2\theta/\omega = 1/1$; refinement method: full-matrix least-squares on $F^2$.

| Description | **2MPDCA** | **3MPDCA** | **3CPDCA** |
|---|---|---|---|
| Chemical formula | $C_9H_9Cl_2NO$ | $C_9H_9Cl_2NO$ | $C_8H_6Cl_3NO$ |
| Formula mass, g mol$^{-1}$ | 218.07 | 218.07 | 238.49 |
| Temperature, K | 293(2) | 299(2) | 304(2) |
| Wavelength, pm | 71.073 | 71.069 | 71.069 |
| Crystal system | monoclinic | orthorhombic | orthorhombic |
| Space group | $P2_1/n$ | $P2_12_12_1$ | *Pnma* |
| *a*, Å | 4.7059(5) | 4.759(1) | 9.935(1) |
| *b*, Å | 11.600(1) | 10.543(3) | 6.997(1) |
| *c*, Å | 18.918(2) | 20.205(5) | 14.140(2) |
| $\alpha$, deg. | 89.881(9) | 90 | 90 |
| $\beta$, deg. | 94.702(9) | 90 | 90 |
| $\gamma$, deg. | 90.012(8) | 90 | 90 |
| Volume, Å$^3$ | 1029.2(2) | 1013.8(4) | 982.9(2) |
| *Z* | 4 | 4 | 4 |
| Density (calculated), g cm$^{-3}$ | 1.407 | 1.429 | 1.612 |
| Absorption coefficient, cm$^{-1}$ | 5.90 | 5.99 | 8.88 |
| *F*(000) | 448 | 448 | 480 |
| Crystal size, mm$^3$ | $0.60 \times 0.07 \times 0.06$ | $4.20 \times 0.30 \times 0.20$ | $0.56 \times 0.25 \times 0.08$ |
| $\theta$ Range, deg. | 4.12 to 25.68 | 2.02 to 24.97 | 2.51 to 26.02 |
| Index ranges | $-5 \le h \le 3$, $-14 \le k \le 14$, $-22 \le l \le 22$ | $0 \le h \le 5$, $-12 \le k \le 10$, $-24 \le l \le 24$ | $-1 \le h \le 12$, $-1 \le k \le 8$, $-4 \le l \le 17$ |
| Reflections collected | 6485 | 3863 | 1763 |
| Independent reflections | 1931 | 1782 | 1763 |
| *R*(int) | 0.0458 | 0.0100 | 0.0000 |
| Completeness to $2\theta$ | 99.0% | 100.0% | 99.6% |
| Max. and min. transmission | – | 0.897 and 0.834 | 0.9324 and 0.6362 |
| Absorption correction | – | analytical | – |
| Data | 1931 | 1782 | 1763 |
| Restraints/parameters | 2/137 | 0/125 | 0/79 |
| Goodness-of-fit on $F^2$ | 0.883 | 1.070 | 1.033 |
| Final $R$ $[I > 2\theta(I)]$ | $R1 = 0.0390$, $wR2 = 0.0714$ | $R1 = 0.0374$, $wR2 = 0.0904$ | $R1 = 0.0581$, $wR2 = 0.1465$ |
| *R* Indices (all data) | $R1 = 0.1116$, $wR2 = 0.0843$ | $R1 = 0.0389$, $wR2 = 0.0920$ | $R1 = 0.0855$, $wR2 = 0.1689$ |
| Absolute structure parameter | – | 0.26(10) | – |
| Extinction coefficient | – | 0.025(3) | 0.018(3) |
| Largest diff. peak and hole, eÅ$^{-3}$ | 0.202 and −0.242 | 0.384 and −0.302 | 0.533 and −0.402 |

report herein our results on the crystal structure studies of the compounds *N*-(2-methylphenyl)-2,2-dichloro-acetamide, 2-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**2MPDCA**); *N*-(3-methylphenyl)-2,2-dichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**3MPDCA**) and *N*-(3-chlorophenyl)-2,2-dichloro-acetamide, 3-$ClC_6H_4NH$-CO-$CHCl_2$ (**3CPDCA**). The results have been analyzed along with our earlier crystal structure studies of the amides, *N*-(phenyl)-2,2-dichloro-acetamide, $C_6H_5NH$-CO-$CHCl_2$ (**PDCA**) [13]; *N*-chloro-*N*-(phenyl)-2,2-dichloro-acetamide, $C_6H_5NCl$-CO-$CHCl_2$ (**NCPDCA**) [9]; *N*-(4-methylphenyl)-2,2-dichloro-acetamide, 4-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**4MPDCA**); *N*-(2-chlorophenyl)-2,2-dichloro-acetamide, 2-$ClC_6H_4NH$-CO-$CHCl_2$ (**2CPDCA**); *N*-(4-chlorophenyl)-2,2-dichloro-acetamide, 4-$ClC_6H_4NH$-CO-$CHCl_2$ (**4CPDCA**) [13]. The results have also been compared and correlated with the crystal structure data of trichloro-acetamide analogues of the general formula 2/3/4-$XC_6H_4NH$-CO-$CCl_3$ (X = $CH_3$ or Cl) [18]: *N*-(phenyl)-2,2,2-trichloro-acetamide, $C_6H_5NH$-CO-$CCl_3$ (**PTCA**); *N*-(2-methylphenyl)-2,2,2-trichloro-acetamide, 2-$CH_3C_6H_4NH$-CO-$CCl_3$ (**2MPTCA**); *N*-(3-methylphenyl)-2,2,2-trichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-$CCl_3$ (**3MPTCA**); *N*-(4-methylphenyl)-2,2,2-trichloro-acetamide, 4-$CH_3C_6H_4NH$-CO-$CCl_3$ (**4MPTCA**); *N*-(2-chlorophenyl)-2,2,2-trichloro-acetamide, 2-$ClC_6H_4NH$-CO-$CCl_3$

(**2CPTCA**); *N*-(3-chlorophenyl)-2,2,2-trichloro-acetamide, 3-$ClC_6H_4NH$-CO-$CCl_3$ (**3CPTCA**); *N*-(4-chlorophenyl)-2,2,2-trichloro-acetamide, 4-$ClC_6H_4NH$-CO-$CCl_3$ (**4CPTCA**); *N*-chloro-*N*-(phenyl)-2,2,2-trichloro-acetamide, $C_6H_5NCl$-CO-$CCl_3$ (**NCPTCA**) [9] and *N*-(phenyl)-acetamide, $C_6H_5NH$-CO-$CH_3$ (**PA**) [21].

## 2. Experimental

### *2.1. Preparation and Characterization of the Compounds*

The compounds *N*-(2-methylphenyl)-2,2-dichloro-acetamide (**2MPDCA**); *N*-(3-methylphenyl)-2,2-dichloro-acetamide (**3MPDCA**) and *N*-(3-chlorophenyl)-2,2-dichloro-acetamide (**3CPDCA**) were prepared from the corresponding anilines, dichloroacetic acid and phosphoryl chloride (Aldrich, Germany) [3, 7, 13, 20, 22]. The commercial solid anilines were purified by zone refining. The liquids were purified by double distillation. All other reagents employed in the preparations and purification of the amides were of analytical grade. The amides **2MPDCA**, **3MPDCA** and **3CPDCA** were prepared, respectively, by treating 2-methylaniline (*o*-toluidine), 3-methylaniline (*m*-toluidine) and 3-chloroaniline with a clear mixture of dichloro-acetic acid (Aldrich, Germany) phosphoryl chloride under constant stirring. The mixtures were slowly warmed to expel HCl. Excess phosphoryl chloride was hydrolyzed by adding cold water dropwise under ice-cold conditions. The separated solids were filtered under suction, washed thoroughly with water and dried. The amides were recrystallized 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 **2MPDCA**, **3MPDCA** and **3CPDCA** were further characterized by recording their infrared and $^{35}Cl$ NQR spectra.

### *2.2. X-Ray Diffraction Studies*

Good single crystals of **2MPDCA**, **3MPDCA** and **3CPDCA** 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) [23 – 33]. 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, 0.97 Å and 0.98 Å for the $CH_3$, $CH_2Cl$ and $CHCl_2$ groups, respectively. Further experimental conditions for the structure determinations and refinements are given in Table 1.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) of *N*-(2-methylphenyl)-2,2-dichloro-acetamide, 2-$CH_3C_6H_4NH$-CO-$CHCl_2$; *N*-(3-methylphenyl)-2,2-dichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-$CHCl_2$ and *N*-(3-chlorophenyl)-2,2-dichloro-acetamide, 3-$ClC_6H_4NH$-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-$CH_3C_6H_4NH$-CO-$CHCl_2$ | | | | |
| C(4) | 8343(5) | 4379(2) | 3354(1) | 47(1) |
| C(3) | 9582(5) | 5001(2) | 2738(1) | 51(1) |
| Cl(1) | 8437(8) | 4280(2) | 1938(1) | 83(1) |
| Cl(2) | 8421(5) | 6427(2) | 2700(1) | 88(1) |
| Cl(1D) | 9830(50) | 4049(10) | 2131(9) | 82(3) |
| Cl(2D) | 7730(40) | 6248(15) | 2509(11) | 82(3) |
| O(5) | 5790(3) | 4377(2) | 3402(1) | 83(1) |
| N(6) | 10259(5) | 3873(2) | 3805(1) | 45(1) |
| C(7) | 9629(4) | 3258(2) | 4429(1) | 42(1) |
| C(8) | 7869(5) | 3769(2) | 4889(1) | 53(1) |
| C(9) | 7261(5) | 3201(3) | 5499(1) | 66(1) |
| C(10) | 8448(6) | 2142(3) | 5649(1) | 73(1) |
| C(11) | 10213(6) | 1644(2) | 5189(1) | 64(1) |
| C(12) | 10811(4) | 2183(2) | 4564(1) | 45(1) |
| C(13) | 12662(5) | 1605(2) | 4060(1) | 64(1) |
| 3-$CH_3C_6H_4NH$-CO-$CHCl_2$ | | | | |
| Cl(1) | 1275(2) | 3890(1) | −408(1) | 83(1) |
| Cl(2) | 3094(3) | 6187(1) | 240(1) | 95(1) |
| C(3) | 3157(5) | 4524(2) | 261(1) | 45(1) |
| C(4) | 1839(5) | 4085(3) | 913(1) | 43(1) |
| O(5) | −707(4) | 4117(3) | 984(1) | 74(1) |
| N(6) | 3679(4) | 3720(2) | 1362(1) | 42(1) |
| C(7) | 3042(5) | 3292(2) | 2018(1) | 40(1) |
| C(8) | 1127(5) | 3941(3) | 2406(1) | 43(1) |
| C(9) | 542(5) | 3528(3) | 3050(1) | 47(1) |
| C(10) | 1913(7) | 2465(3) | 3282(1) | 57(1) |
| C(11) | 3854(7) | 1836(3) | 2896(2) | 64(1) |
| C(12) | 4425(6) | 2241(3) | 2260(1) | 52(1) |
| C(13) | −1498(7) | 4247(3) | 3474(1) | 64(1) |
| 3-$ClC_6H_4NH$-CO-$CHCl_2$ | | | | |
| C(2) | 5783(4) | 2500 | 1785(3) | 74(2) |
| C(3) | 5107(4) | 2500 | 2748(3) | 52(1) |
| Cl(1) | 5272(2) | 4546(2) | 1167(1) | 123(1) |
| O(4) | 3878(2) | 2500 | 2813(2) | 71(1) |
| N(5) | 5978(3) | 2500 | 3466(2) | 54(1) |
| C(6) | 5720(4) | 2500 | 4456(3) | 49(1) |
| C(7) | 4431(4) | 2500 | 4820(3) | 54(1) |
| C(8) | 4311(4) | 2500 | 5792(3) | 62(1) |
| C(9) | 5373(5) | 2500 | 6396(3) | 70(1) |
| C(10) | 6649(5) | 2500 | 6011(3) | 75(2) |
| C(11) | 6816(4) | 2500 | 5048(3) | 64(1) |
| Cl(12) | 2697(1) | 2500 | 6269(1) | 105(1) |

Table 3. Comparison of crystal structure data of *N*-(2/3/4-substituted-phenyl)-2,2-dichloro-acetamides and -2,2,2-trichloro-acetamides.

| | 2/3/4-$XC_6H_4NH$-CO-$CHCl_2$, X = $CH_3$ (M) or Cl (C) | | | | | | | | | 2/3/4-$XC_6H_4NH$-CO-$CCl_3$, X = $CH_3$ (M) or Cl (C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Description | **PA** | **PDCA** | **NCPDCA** | **2MPDCA** | **3MPDCA** | **4MPDCA** | **2CPDCA** | **3CPDCA** | **4CPDCA** | **PTCA** | **NCPTCA** | **2MPTCA** | **3MPTCA** | **4MPTCA** | **2CPTCA** | **3CPTCA** | **4CPTCA** |
| Crystal system | ortho-rhombic | mono-clinic | mono-clinic | mono-clinic | ortho-rhombic | ortho-rhombic | mono-clinic | ortho-rhombic | mono-clinic | mono-clinic | mono-clinic | ortho-rhombic | ortho-rhombic | mono-clinic | ortho-rhombic | ortho-rhombic | ortho-rhombic |
| Space group | *Pbca* | $P2_1c$ | $P2_1c$ | $P2_1/n$ | $P2_12_12_1$ | *Pbca* | $P2_1c$ | *Pnma* | $P2_1c$ | $P2_1c$ | $P2_1c$ | $P2_12_12_1$ | *Pbca* | $P2_1/c$ | $Pna2_1$ | *Fdd*2 | *Pbca* |
| *Z* | 8 | 4 | 4 | 4 | 4 | 8 | 4 | 4 | 8 | 4 | 4 | 4 | 8 | 8 | 4 | 16 | 8 |
| | | | | | | | | Bond lengths, Å | | | | | | | | | |
| C(r)-C(r), mean | 1.387 | 1.384 | 1.374 | 1.379 | 1.384 | 1.381 | 1.379 | 1.374 | 1.380 | 1.383 | 1.377 | 1.377 | 1.378 | 1.381 | 1.383 | 1.364 | 1.378 |
| min. | 1.366 | 1.369 | 1.353 | 1.368 | 1.379 | 1.378 | 1.368 | 1.357 | 1.362 | 1.373 | 1.365 | 1.363 | 1.371 | 1.375 | 1.368 | 1.335 | 1.368 |
| max. | 1.413 | 1.392 | 1.399 | 1.384 | 1.400 | 1.386 | 1.388 | 1.380 | 1.397 | 1.390 | 1.386 | 1.394 | 1.387 | 1.391 | 1.391 | 1.391 | 1.387 |
| C(ring)-N | 1.426 | 1.425 | 1.437 | 1.429 | 1.433 | 1.427 | 1.418 | 1.422 | 1.408 | 1.424 | 1.443 | 1.427 | 1.421 | 1.427 | 1.420 | 1.414 | 1.416 |
| N-C(O) | 1.330 | 1.337 | 1.355 | 1.325 | 1.319 | 1.327 | 1.333 | 1.334 | 1.344 | 1.337 | 1.346 | 1.320 | 1.328 | 1.336 | 1.340 | 1.342 | 1.328 |
| C-O | 1.226 | 1.226 | 1.197 | 1.212 | 1.221 | 1.218 | 1.212 | 1.225 | 1.217 | 1.211 | 1.200 | 1.217 | 1.209 | 1.217 | 1.207 | 1.189 | 1.210 |
| C(O)-C(S) | 1.476 | 1.528 | 1.531 | 1.525 | 1.531 | 1.528 | 1.525 | 1.518 | 1.536 | 1.564 | 1.562 | 1.531 | 1.552 | 1.550 | 1.561 | 1.548 | 1.555 |
| C(S)-Cl(1) | – | 1.768 | 1.760 | 1.691 | 1.753 | 1.764 | 1.745 | 1.753 | 1.757 | 1.768 | 1.759 | 1.748 | 1.739 | 1.761 | 1.758 | 1.744 | 1.764 |
| C(S)-Cl(2) | – | 1.764 | 1.770 | 1.734 | 1.754 | 1.761 | 1.773 | 1.753 | 1.764 | 1.762 | 1.770 | 1.754 | 1.735 | 1.763 | 1.769 | 1.732 | 1.767 |
| C(S)-Cl(3) | – | – | – | – | – | – | – | – | – | 1.772 | 1.764 | 1.753 | 1.751 | 1.770 | 1.770 | 1.737 | 1.743 |
| | | | | | | | | Bond angles, deg. | | | | | | | | | |
| C(2r)-C(1r)-C(6r) | 121.2 | 119.9 | 121.2 | 121.6 | 120.8 | 119.8 | 118.7 | 120.5 | 118.6 | 119.9 | 121.5 | 121.1 | 120.1 | 119.4 | 119.0 | 120.0 | 119.6 |
| C(2r)-C(1r)-N | 115.7 | 122.3 | 118.4 | 118.8 | 120.5 | 118.8 | 120.3 | 122.3 | 117.7 | 122.1 | 119.6 | 119.7 | 122.5 | 119.4 | 119.9 | 122.6 | 122.2 |
| C(6r)-C(1r)-N | 122.7 | 117.8 | 120.3 | 119.6 | 118.6 | 121.4 | 121.0 | 117.2 | 123.8 | 117.9 | 118.8 | 119.2 | 117.3 | 121.2 | 121.1 | 117.4 | 118.1 |
| C(1r)-N-C(O) | 129.3 | 126.8 | 129.2 | 125.1 | 126.0 | 124.4 | 124.7 | 129.2 | 128.4 | 125.4 | 132.3 | 123.7 | 126.9 | 124.1 | 122.4 | 122.2 | 125.6 |
| N-C(O)-C(S) | 117.7 | 113.6 | 113.4 | 114.7 | 114.1 | 114.2 | 114.3 | 113.3 | 112.4 | 114.8 | 118.6 | 115.2 | 113.8 | 116.5 | 114.1 | 114.7 | 114.4 |
| N-C(O)-O | 121.7 | 125.4 | 124.1 | 125.3 | 125.9 | 124.7 | 125.0 | 126.1 | 125.6 | 126.3 | 123.0 | 125.6 | 126.2 | 125.3 | 125.8 | 126.0 | 126.0 |
| O-C(O)-C(S) | 120.4 | 121.0 | 122.5 | 120.1 | 120.0 | 121.0 | 120.7 | 120.6 | 122.0 | 118.9 | 118.3 | 119.2 | 120.0 | 118.2 | 120.1 | 119.3 | 119.6 |
| C(O)-C(S)-Cl(1) | – | 108.1 | 108.9 | 108.7 | 109.8 | 108.6 | 111.1 | 108.6 | 110.5 | 113.4 | 116.1 | D | D | 111.5 | 110.7 | 107.8 | 109.5 |
| C(O)-C(S)-Cl(2) | – | 109.6 | 107.7 | 109.9 | 108.4 | 108.5 | 107.2 | 108.6 | 108.4 | 110.0 | 106.8 | I | I | 108.8 | 108.9 | 109.6 | 108.6 |
| C(O)-C(S)-Cl(3) | – | – | – | – | – | – | – | – | – | 106.9 | 107.9 | S | S | 106.9 | 109.4 | 113.9 | 110.9 |
| Cl(1)-C(S)-Cl(2) | – | 110.8 | 110.5 | 110.0 | 110.8 | 110.2 | 110.4 | 109.5 | 110.7 | 108.4 | 109.5 | O | O | 108.5 | 109.0 | 109.4 | 109.3 |
| Cl(1)-C(S)-Cl(3) | – | – | – | – | – | – | – | – | – | 109.5 | 107.4 | R | R | 109.0 | 108.3 | 108.2 | 108.9 |
| Cl(2)-C(S)-Cl(3) | – | – | – | – | – | – | – | – | – | 108.6 | 109.0 | DER | DER | 109.1 | 110.5 | 108.0 | 109.7 |

Table 4. Comparison of selected dihedral angles (degree) (standard deviations) of *N*-(2/3/4-substituted-phenyl)-2,2-dichloro-acetamides and *N*-(2/3/4-substituted-phenyl)-2,2,2-trichloro-acetamides.

| | Dihedral angle | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2/3/4-$XC_6H_4NH$-CO-$CHCl_2$, X = $CH_3$ (M) or Cl (C) | | | | | | | | 2/3/4-$XC_6H_4NH$-CO-$CCl_3$, X = $CH_3$ (M) or Cl (C) | | | |
| | **PDCA** | **2MPDCA** | **3MPDCA** | **4MPDCA** | **2CPDCA** | **3CPDCA** | **4CPDCA** | | **2MPTCA** | **3MPTCA** | **2CPTCA** | **3CPTCA** |
| Connection | | | | | | | Molecule 1 | Molecule 2 | | | | |
| Cl(1)-C(s)-C(o)-O | 71.3(2) | −66.2(3) | −45.1(3) | 63.3(3) | 42.8(4) | 59.5(2) | 29.1(5) | −29.0(5) | −20.0(8) | 124.3(4) | 1.4(3) | −98.4(9) |
| Cl(2)-C(s)-C(o)-O | −49.5(2) | 54.2(3) | 76.0(3) | −56.5(3) | −77.9(3) | −59.5(2) | −92.6(4) | 92.1(4) | 98.1(7) | 1.6(5) | −118.5(2) | 20.6(1) |
| Cl(3)-C(s)-C(o)-O | – | – | – | – | – | – | – | – | −143.4(7) | −117.2(4) | 120.7(2) | 141.6(8) |
| Cl(1)-C(s)-C(o)-N | −108.3(1) | 113.9(2) | 136.2(2) | −116.8(2) | −139.5(2) | −120.5(2) | −152.6(3) | 152.6(3) | 161.6(6) | −54.3(5) | −177.7(2) | 81.5(7) |
| Cl(2)-C(s)-C(o)-N | 130.9(1) | −125.7(2) | −102.7(2) | 123.4(2) | 99.8(3) | 120.5(2) | 85.7(4) | −86.2(3) | −80.4(7) | −176.9(5) | 62.4(2) | −159.5(6) |
| Cl(3)-C(s)-C(o)-N | – | – | – | – | – | – | – | – | 38.3(7) | 64.3(5) | −58.4(2) | −38.5(9) |
| C(s)-C(o)-N-C(1r) | 178.6(2) | 178.7(2) | 178.5(2) | −178.0(2) | −175.1(3) | 180.0 | −173.1(3) | 175.2(3) | 175.8(5) | 172.7(2) | −179.9(2) | −178.4(7) |
| C(o)-N-C(1r)-C(2r) | −29.7(3) | −48.8(3) | −45.1(4) | 135.4(2) | −134.9(3) | 0.0 | −166.8(4) | 175.7(4) | −57.4(8) | −28.0(4) | −135.2(2) | −36.8(1) |
| C(o)-N-C(1r)-C(6r) | 152.5(2) | 132.1(2) | 136.4(3) | −46.0(3) | 47.2(4) | 180.0 | 16.2(6) | −5.0(6) | 123.9(6) | 155.6(2) | 45.1(3) | 144.8(8) |
| O-C(o)-N-C(1r) | −1.0(3) | −1.1(4) | −0.1(5) | 1.9(4) | 2.5(5) | 0.0 | 5.2(7) | 3.0(7) | −2.5(10) | −5.7(4) | 1.0(3) | 1.4(1) |
| N-C(1r)-C(2r)-C(3r) | −178.0(2) | −179.1(2) | −179.2(2) | 179.2(2) | −177.8(3) | 180.0 | −176.4(3) | −179.3(4) | −178.0(5) | −175.6(2) | −179.4(2) | −179.8(7) |
| N-C(1r)-C(6r)-C(5r) | 177.9(2) | 177.7(2) | 178.9(3) | −179.2(2) | 177.7(3) | 180.0 | 176.7(4) | 179.4(4) | 178.5(5) | 175.6(3) | −179.8(2) | −178.7(8) |
| N-C(1r)-C(2r)-C(me)/Cl | – | −2.6(3) | – | – | 2.6(3) | – | – | – | 0.2(8) | – | 0.8(3) | – |
| C(6r)-C(1r)-C(2r)-C(me)/Cl | – | 178.3(2) | – | – | −179.4(2) | – | – | – | −178.5(6) | – | −179.5(2) | – |
| C(4r)-C(3r)-C(2r)-C(me)/Cl | – | −177.9(2) | – | – | 179.8(2) | – | – | – | 178.0(6) | – | 179.3(2) | – |
| C(1r)-C(2r)-C(3r)-C(me)/Cl | – | – | 178.9(2) | – | – | 180.0 | – | – | – | 178.5(2) | – | −177.4(8) |
| C(5r)-C(4r)-C(3r)-C(me)/Cl | – | – | −177.8(3) | – | – | 180.0 | – | – | – | −178.6(3) | – | 177.5(9) |
| C(6r)-C(5r)-C(4r)-C(me)/Cl | – | – | – | 177.8(3) | – | – | 179.0(3) | 179.8(3) | – | – | – | – |
| C(2r)-C(3r)-C(4r)-C(me)/Cl | – | – | – | −177.8(3) | – | – | −178.5(3) | −179.8(3) | – | – | – | – |

## 3. Results and Discussion

The crystallographic data for the compounds **2MPDCA**, **3MPDCA** and **3CPDCA** are shown in Table 1, while the atomic coordinates and the mean displacement parameters are listed in Table 2. The intramolecular bond distances and angles of **2MPDCA**, **3MPDCA**, **3CPDCA** and of other *N*-(2/3/4-substituted-phenyl)-2,2-dichloro-acetamides and -2,2,2-trichloro-acetamide analogues of these amides and related compounds are compared in Table 3. Table 4 compares the selected dihedral angles of this class of compounds. The hydrogen coordinates, anisotropic displacement parameters and further informations on the crystal structure determinations of **2MPDCA**, **3MPDCA** and **3CPDCA** 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 611815, 239632 and 239750 for *N*-(2-methylphenyl)-2,2-dichloro-acetamide (**2MPDCA**); *N*-(3-methylphenyl)-2,2-dichloro-acetamide (**3MPDCA**) and *N*-(3-chlorophenyl)-2,2-dichloro-acetamide (**3CPDCA**), respectively. 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 throughout the paper. The displacement ellipsoids are drawn at the 50% probability level.

All the three compounds have one molecule each in their asymmetric units, in agreement with the $^{35}$Cl NQR spectra of the compounds [7, 20]. **2MPDCA** crystallizes in the monoclinic symmetry similar to **PDCA**, **NCDCA**, **2CPDCA** and **4CPDCA**, while both

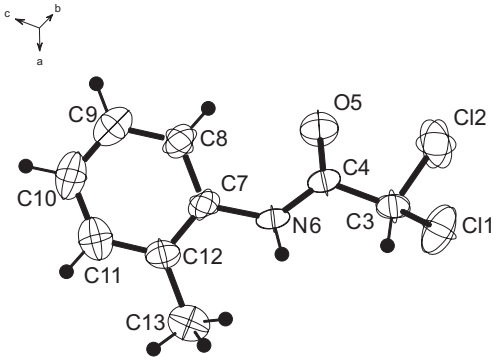


Fig. 1. Molecular geometry of *N*-(2-methylphenyl)-2,2-dichloro-acetamide, 2-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**2MPDCA**), with the numbering of atoms.

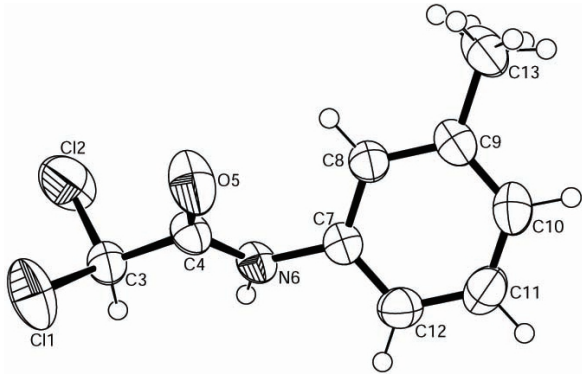


Fig. 2. Molecular geometry of *N*-(3-methylphenyl)-2,2-dichloro-acetamide, 3-$CH_3C_6H_4NH$-CO-$CHCl_2$ (**3MPDCA**), with the numbering of atoms.

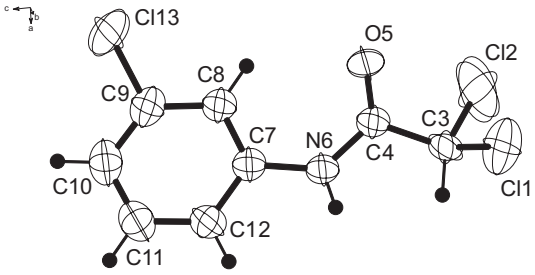


Fig. 3. Molecular geometry of *N*-(3-chlorophenyl)-2,2-dichloro-acetamide, 3-$ClC_6H_4NH$-CO-$CHCl_2$ (**3CPDCA**), with the numbering of atoms.

**3MPDCA** and **3CPDCA** crystallize in the orthorhombic symmetry similar to **PA** and **4MPDCA**. Comparison of the available data in Table 3 reveals that the changes in the side chain lead to changes in the crystal system from orthorhombic to monoclinic on conversion from **PA** to either **PDCA** or **PTCA**, but *N*-chlorination of the latter does not affect the crystal system. Contrary to this, the ring substitutions in **PDCA** and **PTCA** result in different effects. Introduction of either a methyl or Cl group into the benzene ring in **PDCA** at *ortho* position does not change the crystal system, while the introduction of either a methyl or Cl group into the benzene ring in **PTCA** at *ortho* position changes the crystal system from monoclinic to orthorhombic. But the introduction of either a methyl or Cl group into the benzene ring at meta position has an identical effect in both series of compounds. But again, as may be seen in Table 3, the substitutions of chloro and methyl groups at the *para* position have different effects in the two series of compounds. They exactly have reverse effects – the crystal symmetries of the chloro-substituted and methyl-substituted chloro-

acetamides are interchanged on replacement of the side chain -$CHCl_2$ by -$CCl_3$. Only when substitutions are made at *ortho* or *para* position the effects are different. With *meta* substitutions the effect remains the same in both series of compounds either with the methyl or chloro group.

It is difficult to generalize these aspects, unless extensive work is carried out with the other substituents and side chains. The work in this direction is in progress in our group.

We shall now consider the intramolecular geometry of the title compounds. We find that the range of C(*i*)-C(*j*) bond distances within the phenyl rings of the compounds show no significant variations with the substitution either at the side chain or in the phenyl ring. The mean distances of all the compounds lie in the range 1.364 – 1.387 Å, with the minimum ring distance of 1.335 Å for **3CPTCA** and the maximum value of 1.413 Å for **PA**. Also the range of the six ring distances for the compound **PA** is wider (1.366 – 1.413 Å), which narrows down on substitution either in the phenyl ring or at the side chain, the narrowest range being 1.378 – 1.386 Å for **4MPDCA**. The C(ring)-N distance is marginally affected by either ring or side chain substitution. It is enlarged on *N*-chlorination and shortened by chloro substitution in the ring. The C(O)-N bond distance is also enlarged on *N*-chlorination. But there is no particular trend in its variation on ring substitution. The variation of the C-O bond length also does not show a trend. The C(O)-C(side) bond length is also affected on substitution and *N*-chlorination, but there is no specific trend, probably because the amides crystallize in different crystal systems, and thus the distances are differently affected.

As regards the bond angles, the mean ring angles are observed around 120°, although the individual values deviate from 120° by zero to about 3°. C(2ring)-C(1ring)-N and C(6ring)-C(1ring)-N angles differ by 7° for PA, which narrows down to 4.5° and 4.2° for **PDCA** and **PTCA**, respectively. The difference between the two angles undergoes a further change on substitution and it is generally minimum for the *ortho*-substituted compounds. The C(2ring)-C(1ring)-C(6ring) bond angles show similar variations for both the dichloro- and trichloro-substituted side chain series of compounds. The deviation of these from 120° is only by zero to about 1.5°. The C(ring)-*N*-C(O) bond angle generally decreases with either side chain or ring substitution of **PA**, but increases on *N*-chlorination of the compounds. The *N*-C(O)-C(side chain) angles get stabilized around 114° with some exceptions. Similarly the O-C(O)-N angles get stabilized in the range 125° to 126° and the O-C(O)-C(side chain) angles lie around 120°.

Table 4 documents the comparison of selected dihedral angles for both the dichloro and trichloro side chain analogous series of amides. As may be seen, in the case of dichloro side chain-substituted amides, the deviation of the angle, C(s)-C(o)-N-C(1r) from 180° is maximum for ring chloro-substituted compounds and minimum for the methyl-substituted amides, with the exception of **3CPDCA**. The trend is opposite for the trichloro side chain-substituted amides. The sum of the magnitudes of the two angles C(o)-N-C(1r)-C(2r) and C(o)-N-C(1r)-C(6r) is invariably around 180° for all the compounds in both series of amides. The angles *N*-C(1r)-C(2r)-C(3r) and *N*-C(1r)-C(2r)-C(5r) generally lie around 180°.

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