

Structure of (3-Chlorophenoxy)acetic Acid*

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Abstract. $C_8H_7ClO_3$, $M_r = 186.6$, monoclinic, $P2_1/c$, $a = 14.047$ (2), $b = 5.168$ (1), $c = 12.373$ (2) Å, $\beta = 113.93$ (3)°, $V = 821.0$ (1) Å³, D_m (by flotation) = 1.50, $D_x = 1.509$ Mg m⁻³, $Z = 4$, $F(000) = 384$, $\lambda(\text{Mo } K\alpha) = 0.70930$ Å, $\mu(\text{Mo } K\alpha) = 0.42$ mm⁻¹, $T = 293$ K, $R = 0.048$ for 1340 unique observed reflections. This acid forms centrosymmetric cyclic hydrogen-bonded dimers [O...O, 2.609 (2) Å] similar to the majority of the phenoxyalkanoic acids. The oxoacetic acid side chain is essentially coplanar with the benzene ring, with the non-bonding O(ether) to O(carboxyl) distance 2.640 (2) Å.

Introduction. The title compound (3-CPAA) is a member of the phenoxyalkanoic acid series which includes a number of herbicidally active ring-substituted acetic and 2-propanoic acid analogues. 3-CPAA is inactive (Synerholm & Zimmerman, 1945), and provides another example of a *meta*-substituted acid. The structure of a related compound, 2-(3-chlorophenoxy)propanoic acid (3-CPAA) (Mak, Smith & Kennard, 1986) has already been published.

Experimental. Colourless prismatic crystals of 3-CPAA obtained by recrystallization from toluene. A single crystal (0.30 × 0.25 × 0.15 mm) was used to collect intensity data on an Enraf–Nonius CAD-4 diffractometer. 20 reflections ($8 < \theta < 20^\circ$) used for lattice-parameter determinations. Systematic absences [0*k*0 ($k = 2n + 1$); *h*0*l* ($l = 2n + 1$)] indicated $P2_1/c$. Data corrected for absorption and decay (−5.3% in 40.5 hours). Range of data: *h* (0 to 16), *k* (0 to 6), *l* (−14 to +14) up to $\theta_{\text{max}} 24.0^\circ$, $2\theta/\omega$ scan. Three standards used [006; 17 491 (5); 900; 25 348 (8); 020; 70 450 (25)]. Transmission: min. 57.2; max. 99.4; mean 77.2%. 2004 reflections measured, of which 1340

with $I > 2.5\sigma(I)$ were unique (249 unobserved) and used in the structure determination; structure from *E* map by multiresolution Σ_2 sign expansion direct methods of *SHELX76* (Sheldrick, 1976). Blocked-matrix least-squares refinement (*F*'s) with anisotropic thermal parameters on all non-hydrogens (H atoms isotropic) gave $R = 0.048$ and $wR = 0.052$ with $w = 1.0/[\sigma^2(F_o) + 0.0025F_o^2]$. The H atoms were all located from a difference Fourier map and their positional and isotropic thermal parameters refined. Max., av. Δ/σ in the final cycle were 1.0, 0.8. Max. peak in final difference Fourier map 0.18 e \AA^{-3} above a background of 0.11 e \AA^{-3} . Table 1 lists the atomic parameters‡ while bond distances and angles are given in Table 2.

The computer programs used were *CAD-4*, Fortran Version 4 Mod. D (van Meurs, 1985) and *SDP-Plus* V2.2 (Frenz, 1984) for collecting and processing data and *SHELX76* (Sheldrick, 1976), for structure determination, with the scattering factors for C, H and Cl included in the program. These were run on DEC microVAX and IBM 3083 computers respectively. *APPLECRYST83* (Kennard, 1983) was used to determine the molecular geometry.

Discussion. The molecules of 3-CPAA adopt a conformation comparable with other phenoxyacetic acids, with the side chain essentially coplanar with the phenoxy residue [torsion angle C(1)–O(7)–C(8)–C(9), $+174.6$ (2)°], regardless of the position and nature of the ring substituent (Table 3). This is in contrast with the 2-(phenoxy)propanoic acids, e.g. the analogous acid 3-CPPA (Mak, Smith & Kennard,

‡ Lists of structure factors, hydrogen coordinates, and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43058 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Systematic name: 3-chlorophenoxyethanoic acid.

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Table 1. Atomic parameters ($\times 10^4$) with estimated standard deviations in parentheses, and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
C(1)	2581 (1)	2975 (3)	385 (2)	39 (1)
C(2)	1914 (1)	4494 (4)	-536 (2)	39 (1)
C(3)	1305 (1)	6305 (3)	-294 (2)	39 (1)
Cl(3)	490 (1)	8239 (1)	-1447 (1)	51.4 (3)
C(4)	1341 (2)	6649 (4)	830 (2)	51 (1)
C(5)	2013 (2)	5118 (5)	1730 (2)	55 (1)
C(6)	2647 (2)	3282 (4)	1523 (2)	46 (1)
O(7)	3164 (1)	1236 (3)	68 (1)	47 (1)
C(8)	3809 (2)	-423 (4)	968 (2)	39 (1)
C(9)	4323 (1)	-2378 (4)	488 (2)	35 (1)
O(10)	4143 (1)	-2367 (3)	-601 (1)	46 (1)
O(11)	4908 (1)	-3956 (3)	1223 (1)	46 (1)

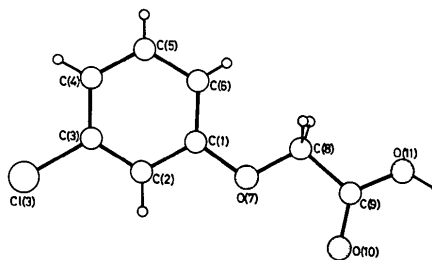


Fig. 1. Molecular conformation and atom-numbering scheme for 3-CPAA.

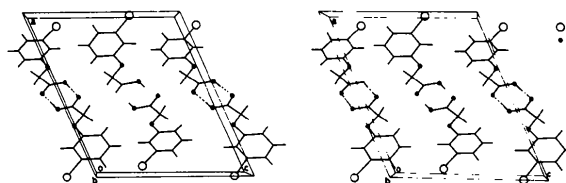


Fig. 2. Stereoview of the packing of 3-CPAA in the unit cell viewed down b .

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

C(1)—C(2)	1.388 (2)	C(5)—C(6)	1.394 (4)
C(1)—C(6)	1.382 (3)	O(7)—C(8)	1.406 (2)
C(1)—O(7)	1.376 (3)	C(8)—C(9)	1.497 (3)
C(2)—C(3)	1.380 (3)	C(9)—O(10)	1.267 (3)
Cl(3)—C(3)	1.738 (2)	C(9)—O(11)	1.250 (2)
C(3)—C(4)	1.382 (4)		
C(4)—C(5)	1.380 (3)		
C(6)—C(1)—C(2)	121.0 (2)	C(5)—C(6)—C(1)	118.8 (2)
O(7)—C(1)—C(2)	114.7 (2)	C(8)—O(7)—C(1)	116.1 (2)
O(7)—C(1)—C(6)	124.3 (2)	C(9)—C(8)—O(7)	110.9 (2)
C(3)—C(2)—C(1)	118.4 (2)	O(10)—C(9)—C(8)	120.0 (2)
Cl(3)—C(3)—C(2)	118.1 (2)	O(11)—C(9)—C(8)	115.6 (2)
C(4)—C(3)—C(2)	122.2 (2)	O(11)—C(9)—O(10)	124.4 (2)
C(4)—C(3)—Cl(3)	119.6 (2)		
C(5)—C(4)—C(3)	118.1 (2)		
C(6)—C(5)—C(4)	121.4 (2)		

Table 3. Comparative structural data for related phenoxyalkanoic acids

Compound	PAA	2-CPAA	3-CPAA	4-CPAA	3-CPAA
Reference	Kennard, Smith & White (1982)	Kennard & Smith (1981)	This work	Kennard, Smith & White (1981)	3-CPAA Mak, Smith & Kennard (1986)
Distances (\AA)					
O—H...O	2.629(4)	2.628(10); 2.651(10)	2.609(2)	2.600(3)	2.669(4)
O(7)—O(10)	2.671(4)	2.643(10); 2.637(10)	2.640(2)	2.672(3)	2.754(4)
Dihedral angle ($^\circ$)					
Benzene	4.7(3)	5.6(8); 8.2(8)	5.2(3)	3.3(4)	87.3(5)
Torsion angles ($^\circ$)					
C(2)—C(1)	+176.1(2)	-179.4(8); +179.9(8)	-176.9(2)	+179.2(4)	-174.0(2)
O(7)—C(1)	-175.1(2)	-175.1(8); -173.2(8)	+174.6(2)	+178.5(4)	-74.5(2)
C(1)—O(7)	+179.2(2)	-179.3(9); -179.9(8)	-179.5(2)	+177.7(4)	+154.0(2)
O(7)—C(8)					
-C(9)—O(11)					

PAA = phenoxyacetic acid

PPA = 2-(phenoxy)propanoic acid

CPAA = chlorophenoxyacetic acid

3-CPAA = 2-(3-chlorophenoxy)propionic acid

1986), which, without exception, adopt a synclinal side-chain conformation. Interatomic distances, angles and other structural features are also comparable to the mono-substituted phenoxyacetic acids (see Table 3), including the synplanar placement of the 'carbonyl' oxygen [O(10)] of the carboxylic acid group [torsion angle O(7)—C(8)—C(9)—O(1), $-0.2(2)^\circ$], giving an O(7)...O(10) interactive distance of 2.640 (2) \AA .

Molecules of 3-CPAA (Fig. 1) form the usual centrosymmetric hydrogen-bonded cyclic dimers [O...O, 2.609 (2) \AA] (Fig. 2), with no other significant interdimer associations.

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Structure of 3-Methylxanthine

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Abstract. $C_6H_6N_4O_2$, $M_r = 166.1$, monoclinic, $P2_1/c$, $a = 3.742(5)$, $b = 14.710(8)$, $c = 12.159(8) \text{ \AA}$, $\beta = 96.8(1)^\circ$, $U = 666.5 \text{ \AA}^3$, $Z = 4$, $D_x = 1.66 \text{ g cm}^{-3}$, Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$, $\mu = 0.84 \text{ cm}^{-1}$, $F(000) = 344$, $T = 293 \text{ K}$, $R = 0.058$ for 957 unique reflections. The molecules form base-paired hydrogen-bonded dimers, with each molecule involved in four H bonds. The base ring is planar within experimental error. Propeller twist is absent.

Introduction. The structure of 3-methylxanthine was studied as part of an investigation into the self base-pairing of nucleic acid constituents. Of especial interest is the propeller twist of the base pair (Dickerson, 1983), this being the angle between the base planes about an axis joining them. Wilson (1985) has investigated the propeller twist for a number of such compounds.

Experimental. Crystals of a suitable size were produced by forming a saturated solution of 3-methylxanthine in water at 353 K. This solution was then allowed to stand in a water bath at 303 K for several days. The resulting crystals had a prismatic habit elongated along **a**. Space group and initial cell dimensions were obtained from Weissenberg photographs. These Weissenberg photographs also showed evidence of very strong thermal diffuse scattering. Refined cell dimensions measured on a Stoe Stadi 2 two-circle diffractometer using crystals mounted along **a** and **b**.

Intensities measured on the diffractometer using an **a**-axis-mounted crystal of dimensions $0.6 \times 0.3 \times 0.3 \text{ mm}$. Range of indices $0 < h < 3$, $-18 < k < 18$, $-15 < l < 15$; $\theta_{\text{max}} = 27^\circ$. Standard reflections, which showed less than 5% variation, measured every 100 measurements. No absorption corrections applied.

3421 reflections measured, 957 unique with $I > 3\sigma I$ regarded as observed, $R_{\text{int}} = 0.018$, the $\bar{1}12$ reflection was not used in the refinement on grounds of extinction. Structure solved by Patterson methods using *PATMET* (Wilson & Tollin, 1985). Refinement (on F) by full-matrix least squares with *SHELX76* (Sheldrick, 1976). H-atom positions obtained from difference Fourier map. Non-H atoms refined anisotropically. H atoms included as fixed atoms with isotropic temperature factor of 0.08 \AA^2 . 109 parameters refined, $R = 0.058$, $wR = 0.080$, $w = 1.8044[\sigma(F)^2 + 0.002362F^2]$. Max. $\Delta/\sigma = 0.013$, max. difference map peak 0.4 , min. -0.39 e \AA^{-3} . The largest of these peaks is close to the methyl C atom and suggests that there may be a degree of rotational disorder in the methyl H-atom positions. Other programs used: *XANADU* (Roberts & Sheldrick, 1975) and *PLUTO* (Motherwell & Clegg, 1978). Scattering factors from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction.

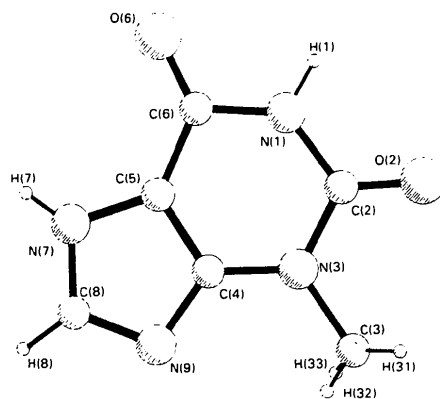


Fig. 1. View of the molecule showing the atom numbering.