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(4-Chlorophenoxy)acetic Acid

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Abstract. C₈H₇ClO₃, m.p. 431 K, $M_r = 186.5$, $P\bar{1}$, $a = 8.117$ (5), $b = 7.399$ (5), $c = 7.113$ (4) Å, $\alpha = 85.91$ (6), $\beta = 71.73$ (6), $\gamma = 88.03$ (6)°, $V = 404.6$ Å³, $Z = 2$, $D_x = 1.53$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.435$ mm⁻¹, $R = 0.048$, 1132 observed reflexions. The molecules form planar centrosymmetric hydrogen-bonded cyclic dimers [O...O, 2.600 (3) Å] about a centre of symmetry at $(1, \frac{1}{2}, \frac{1}{2})$ in the cell. This conformation is similar to that of the parent acid phenoxyacetic acid and the isomeric (2-chlorophenoxy)acetic acid.

Introduction. The synthesis and herbicidal properties of (4-chlorophenoxy)acetic acid (4-CPA) were first reported by Synerholm & Zimmerman (1945). It has the highest activity among the monochlorophenoxy acids (Garraway & Wain, 1976). Because of its low water solubility it has utility, along with (3,4-dichlorophenoxy)acetic acid, as a wettable powder or paste for direct application to soil as a pre-emergence herbicide (Crafts, 1957). Apart from the herbicidal properties of the parent acid, various salts and derivatives of 4-CPA have useful therapeutic properties and are in common medical usage. Amphetamine (4-chlorophenoxy)acetate is used as an anorexigenic agent (Satiety!); (4-chlorophenoxy)acetic acid 2-isopropylhydrazide (Iproclozide) finds use as a monoamine oxidase inhibitor while (4-chlorophenoxy)acetic acid 2-(dimethylamino)ethyl ester (Meclofenoxate) is an analeptic and also possesses plant-growth regulating properties (Merck, 1968). The structure of the title compound was determined as part of a systematic investigation of the

structural and conformational aspects of the phenoxyalkanoic acids.

Although the preferred conformation for the phenoxyacetic acids is planar (Kennard, Smith & White, 1981), anomalous examples exist, e.g. (2,4-dichlorophenoxy)acetic acid (2,4-D) and (2,5-dichlorophenoxy)acetic acid (2,5-D), both powerful herbicides. The (4-chlorophenoxy)acetic radical in the complex diaquabis[(4-chlorophenoxy)acetato]copper(II) has also been found to be planar (Smith, O'Reilly, Kennard, Stadnicka & Oleksyn, 1981).

The compound was synthesized from sodium 4-chlorophenoxide and ethyl bromoacetate using the general procedure of Synerholm & Zimmerman (1945). Colourless prismatic crystals suitable for X-ray work were grown from a benzene-acetone mixture. 1135 reflexions with $I > 2.5\sigma(I)$ were considered observed out of 1441 collected from one crystal (0.45 × 0.30 × 0.12 mm) on a Syntex $P\bar{1}$ four-circle diffractometer ($2\theta_{\text{max}} = 50^\circ$, Mo $K\alpha$) (graphite monochromator). No corrections were made for absorption [$\mu(\text{Mo } K\alpha) = 0.435$ mm⁻¹]. The structure was solved by multisolution \sum_2 sign expansion (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms reduced $R [= \sum \|F_o - F_c\| / \sum F_o]$ from an initial value of 0.44 to 0.048 and $R_w [= (\sum w \|F_o - F_c\|^2 / \sum w F_o^2)^{1/2}]$ to 0.055 [$w = 2.71/\sigma^2 F_o + 6.11 \times 10^{-4} (F_o)^2$]. H positions were located in a difference-Fourier synthesis and included in the refinement at fixed positions with their isotropic U values set invariant at 0.05 Å². Three intense low-angle reflexions (111, $\bar{1}20$, $2\bar{1}1$) were

Table 1. Atomic positional parameters ($\times 10^4$) and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

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

	x	y	z	B_{eq} (\AA^2)
Cl(4)	1419 (1)	729 (1)	7833 (1)	4.7 (1)
O(7)	6127 (3)	2975 (3)	-34 (3)	3.8 (1)
O(10)	8187 (3)	3812 (3)	-3719 (3)	4.2 (1)
O(11)	9931 (3)	5389 (4)	-2583 (4)	4.5 (1)
C(1)	5103 (4)	2474 (4)	1837 (5)	3.0 (2)
C(2)	3660 (4)	1489 (5)	1980 (5)	3.6 (2)
C(3)	2540 (4)	929 (5)	3806 (5)	3.9 (2)
C(4)	2850 (4)	1411 (4)	5503 (5)	3.4 (2)
C(5)	4298 (4)	2372 (4)	5401 (5)	3.3 (2)
C(6)	5420 (4)	2934 (4)	3560 (5)	3.4 (2)
C(8)	7605 (4)	4009 (5)	-216 (5)	3.5 (2)
C(9)	8598 (4)	4395 (4)	-2364 (5)	3.3 (2)
H(2)	3318	614	909	
H(3)	1561	213	3875	
H(5)	4351	2657	6845	
H(6)	3605	6554	6303	
H(81)	8539	3374	350	
H(82)	7356	5147	825	
H(11)	10345	5643	-3496	

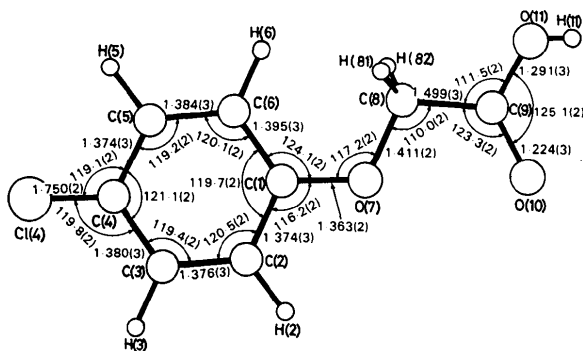


Fig. 1. Molecular conformation and atom-naming scheme with bond distances (\AA) and angles ($^\circ$).

considered to be seriously affected by extinction and removed before the final cycle of refinement. A final difference-Fourier synthesis revealed no features greater than 0.15 e \AA^{-3} . Neutral-element scattering factors were used for the non-H atoms (Doyle & Turner, 1968); those for H were the Stewart, Davidson & Simpson (1965) values. Atomic positional parameters are given in Table 1.* Interatomic distances and angles are shown in Fig. 1.

Discussion. The molecules of (4-chlorophenoxy)acetic acid form the usual hydrogen-bonded cyclic dimers [$\text{O} \cdots \text{O}$, $2.600(3) \text{ \AA}$] (Fig. 2). This compound is

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35918 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

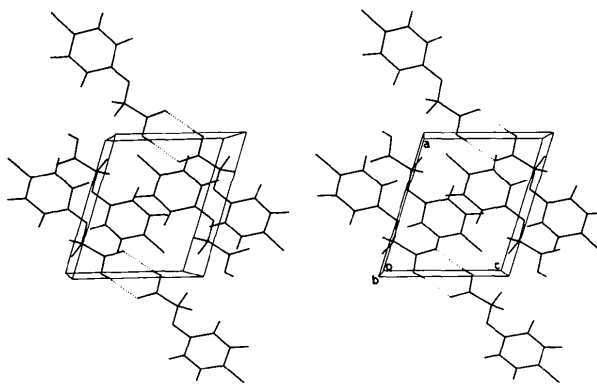


Fig. 2. Stereoview down the *b* axis.

structurally similar to the parent phenoxyacetic acid (Kennard *et al.*, 1981) both in bond distance and angular parameters, and in the molecular conformation. The torsion angles about the C(1)–O(7), O(7)–C(8) and C(8)–C(9) vectors [C(2)–C(1)–O(7)–C(8), C(1)–O(7)–C(8)–C(9), O(7)–C(8)–C(9)–O(11)] are $+179.2(4)$, $+178.5(4)$ and $+177.7(4)^\circ$ respectively compared with $+176.1(2)$, $-175.1(2)$, $+179.2(2)^\circ$ for the comparable angles in the parent acid. The location of the proton on the carboxylic acid oxygen O(11) and the magnitudes of the angular distortion of the C–C–O angles in the carboxylic acid group [C(8)–C(9)–O(10), $123.3(2)$; C(8)–C(9)–O(11), $111.5(2)^\circ$] confirm the usual synplanar–synplanar (carbonyl) conformational motif found for the series of phenoxyacetic acids. Despite the existence of a delocalized proton intermediate between the two carboxylate oxygens in phenoxyacetic acid, a similar angular distortion exists [$121.1(2)$, $114.8(2)^\circ$] although the C–O distances are equal [$1.266(3)$, $1.260(3) \text{ \AA}$].

The same gross molecular conformation and angular distortion about the oxyacetic acid side chain and the *exo*-C(1) ring angles is also found for the phenoxyacetate ligand in the complexed state, irrespective of the mode of complexation. In diaquabis(4-chlorophenoxy)acetato]copper(II) (Smith, O'Reilly, Kennard, Stadnicka & Oleksyn, 1981), the phenoxy ligand chelates *via* the ether and carboxyl oxygens and is close to planar with similar intra-ligand angles to 4-CPA. A confident prediction may also be made about similar features existing in the complex diaquabis(4-chlorophenoxy)acetato]zinc(II), which is isostructural with diaquabis(phenoxyacetato)zinc(II) (Smith, O'Reilly, Kennard, Stadnicka & Oleksyn, 1981). The last compound has planar bidentate coordination *via* asymmetric Zn–O bonds to carboxyl oxygens. The same situation exists in the series of Mg^{II} , Mn^{II} and Co^{II} complexes of (4-chlorophenoxy)acetic acid, also isostructural with the phenoxyacetic acid complexes involving bridging carboxyl groups in a two-

dimensional polymeric mode (Smith, O'Reilly & Kennard, 1980).

Packing of the dimer units in the cell is such that an unusually close intermolecular H...H contact exists between symmetry-related ring protons [H(3)...H(3')] (2.55 Å). However, this does not appear to perturb the ring system in any way nor does it lead to any unusual effects in the temperature factors of the associated atoms.

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2,3:4,6-Di-*O*-isopropylidene-5-thio- α -D-glucopyranose

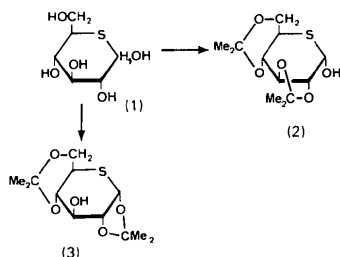
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Abstract. C₁₂H₂₀O₅S, *M_r* = 276.4, monoclinic, *P*2₁, *a* = 5.949 (1), *b* = 13.082 (4), *c* = 9.028 (2) Å, β = 94.71 (1)°, *U* = 700.2 Å³, *Z* = 2, *D_x* = 1.311 Mg m⁻³; final *R* = 0.068 for 1326 unique diffractometer data. A S-containing pyranoid ring with a chair conformation is *trans*-fused to a 1,3-dioxolane ring system which has an envelope conformation.

Introduction. The compound (2) was obtained by reaction of 5-thio-D-glucose (1) with acetone and 2,2-dimethoxypropane (Clegg, Hughes & Al-Masoudi, 1979). The crystal structure was determined to verify that the product was the *trans*-fused system (2) rather than the *cis*-fused isomer (3).



Intensities were collected in the $2\theta/\omega$ scan mode on a Hilger & Watts Y290 diffractometer with Mo *K α* radiation (λ = 0.71069 Å) and a Zr filter. Cell dimensions and the crystal-orientation matrix were obtained by least-squares refinement from 12 reflexions with $2\theta > 40^\circ$. 1326 unique data with $2\theta \leq 55^\circ$ and $I > 0$, corrected for crystal decomposition (assessed by periodic measurement of three standard reflexions, which showed a total decay of intensity of *ca* 35%) but not for absorption (μ = 0.23 mm⁻¹), were used for structure determination.

The structure was determined by a multi-solution tangent-refinement method and refined to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma^2(F_o)$]. The H atom of the OH group was refined freely; all other H atoms were constrained [C–H = 0.96 Å, H–C–H = 109.5°; the H–C vector for X₃CH lies along the vector sum of the three C–X unit vectors; $U(H) = 1.1U_{eq}(C)$]. Anisotropic thermal parameters were refined for C, O and S. The *y* coordinate of S(1) was fixed to define the origin. Final values of *R* and *R_w* [$= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$] are 0.068 and 0.062 respectively. Atom coordinates, and bond lengths and angles