Fig. 3. Projection of the crystal structure down the *b* axis.

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(4-Chlorophenoxy)acetic Acid

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Abstract. $C_8H_7ClO_3$, triclinic, $P\bar{1}$, $Z = 2$, $a = 7\cdot108$ (1), $b = 7\cdot407$ (1), $c = 8\cdot1217$ (6) Å, $\alpha = 88\cdot11$ (1), $\beta = 108\cdot24$ (1), $\gamma = 94\cdot05$ (1)°, $V = 405\cdot1$ Å^3, $\rho_c = 1\cdot531$, $\rho_m = 1\cdot525$ g cm^{-3}, $M_r = 186\cdot6$, m.p. $= 433 \pm 1$ K. The structure was solved by the heavy-atom method and refined by full-matrix least squares to an R value of 0·059 for 819 observed reflections. The molecules dimerize about a centre of symmetry, as is usual with simple carboxylic acids, and are linked by a pair of hydrogen bonds with O$\cdots$O 2·610 (7) Å. A short intermolecular Cl$\cdots$Cl distance 3·349 (3) Å was observed.

Introduction. (4-Chlorophenoxy)acetic acid, a potent auxin, was crystallized from methanol by slow evaporation. A crystal of dimensions 0·15 × 0·45 × 0·48 mm was mounted on a Nonius CAD-4 diffractometer and the cell parameters were refined by a least-squares method from the measured angular settings of 24 well centred reflections lying in the θ range 16–44°. Data were collected at room temperature in the ω–2θ scan mode with graphite-monochromatized Cu $K\alpha$ radiation. Three standard reflections, well distributed in reciprocal space, were monitored for every 50 min of data collection and their intensities did not show any systematic change. 1186 independent reflections in the θ range 2–60° were measured and 819 reflections were considered above threshold at the $2\cdot75\sigma(I)$ level of significance. The intensities were corrected for Lorentz and polarization effects, but not for absorption [μ(Cu $K\alpha$) = 3·95 mm^{-1}].

The scale factor to place the data on the absolute scale and the overall temperature factor ($B = 2\cdot5$ Å^2) were determined from a Wilson plot. The $N(z)$ statistical test indicated a centre of symmetry in the unit cell. The Patterson map was completely interpreted for intramolecular vectors and the Fourier map taken with the Cl position alone ($R = 0\cdot54$) revealed a major fragment of the molecule. One more Fourier synthesis gave the complete molecule ($R = 0\cdot25$). The positions of all H atoms, including the one participating in the dimer formation, were obtained from a difference Fourier map (at $R = 0\cdot09$). Further refinement by

Table 1. *Fractional coordinates (for non*-H ×10⁴, *for* H ×10³) *and isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}/B_{iso} (Å²)
Cl	12831 (3)	−5728 (3)	−1416 (2)	4·29 (8)
C(1)	10536 (10)	−6393 (10)	−2844 (8)	3·3 (2)
C(2)	8777 (11)	−5936 (11)	−2561 (9)	3·6 (2)
C(3)	7006 (10)	−6463 (10)	−3646 (9)	3·3 (2)
C(4)	6815 (9)	−7498 (9)	−5127 (8)	2·7 (2)
C(5)	8578 (10)	−7926 (10)	−5396 (9)	3·2 (2)
C(6)	10393 (9)	−7397 (10)	−4318 (9)	3·2 (2)
O(1)	4967 (6)	−7964 (6)	−6126 (5)	3·2 (1)
C(7)	4761 (10)	−9025 (11)	−7622 (9)	3·0 (2)
C(8)	2674 (10)	−9378 (10)	−8583 (9)	3·4 (2)
O(2)	1267 (7)	−8808 (7)	−8202 (6)	4·0 (2)
O(3)	2409 (7)	−10406 (7)	−9945 (6)	4·1 (2)
H(1)	1144 (11)	−770 (10)	−451 (10)	2·9 (4)
H(2)	897 (12)	−529 (11)	−169 (10)	2·7 (4)
H(3)	580 (10)	−609 (10)	−357 (9)	2·8 (3)
H(4)	842 (11)	−858 (11)	−610 (10)	2·5 (3)
H(5)	472 (10)	−1017 (11)	−720 (9)	2·3 (3)
H(6)	463 (10)	−842 (11)	−839 (9)	2·3 (3)
H(7)	79 (11)	−1085 (11)	−1072 (9)	3·1 (3)

full-matrix least squares of all the atoms reduced R to 0·059 for the observed reflections. The H atoms were given the temperature factors of the atoms to which they are bonded. Final F_o and ΔF syntheses did not show any unexplainable electron densities. The scattering-factor curves were taken from *International Tables for X-ray Crystallography* (1962). The coordinates of all the atoms along with their B_{eq} values are listed in Table 1.*

Discussion. The bond lengths and angles are given in Figs. 1 and 2 respectively, and they are in good agreement with those found in other substituted phenoxyacetic acids (Vijay Kumar & Rao, 1980). The two molecules are hydrogen bonded [O(3)—H···O(2) 2·610 (7) Å] through their carboxyl groups to form dimers and the hydrogen-bond length is comparable with the values observed in other cyclic dimers. The geometry of the carboxyl group is in good agreement with those of the other carboxylic acids which show significant differences in their C—O lengths [1·240 (9) and 1·322 (9) Å] and C—C—O angles [125·4 (7) and 112·3 (6)°].

After the acceptance of this work for publication, the structure of (4-chlorophenoxy)acetic acid by Kennard, Smith & White (1981) appeared. The bond lengths and
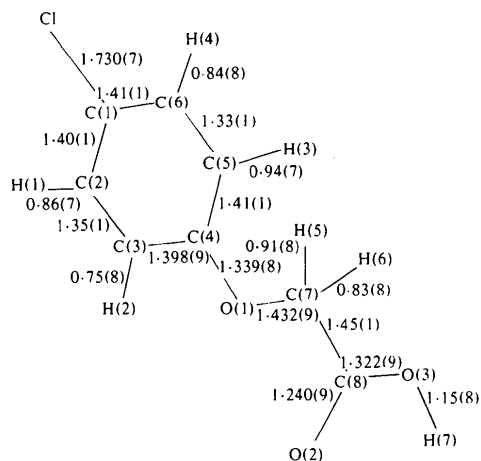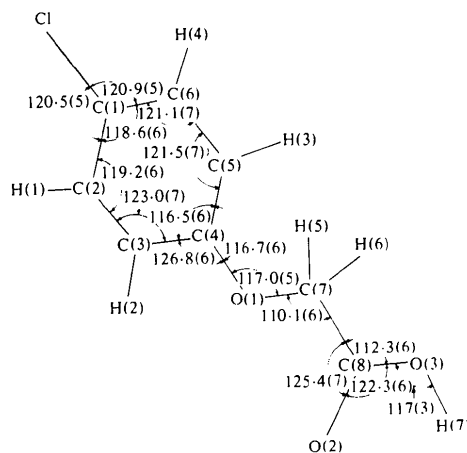

Fig. 1. Bond lengths (Å) with e.s.d.'s in parentheses.

Fig. 2. Bond angles (°) with e.s.d.'s in parentheses.

angles reported there compare well with those of the present work except for the C(7)—C(8) length and five angles which differ by 3σ–5σ. The C(7)—C(8) bond length is 1·45 (1) Å compared to 1·499 (3) Å in the earlier report. Similar shortening of this bond was observed in (4-nitrophenoxy)acetic acid [1·48 (1) Å] (Vijay Kumar & Rao, 1980) and also in (2-chlorophenoxy)acetic acid [1·48 (2) Å] (Kennard & Smith, 1981). The large difference in C—C—O angles [13·1 (9) °] of the carboxyl group found in this study has been corroborated by the earlier work, but the smaller difference in the C—O bonds, 1·224 (3) and 1·291 (3) Å, observed earlier does not seem to be consistent with the large difference in the C—C—O angles.

Thimann (1969) has postulated that the auxin properties in the case of phenoxy-type molecules are critically dependent on the separation of the O atom of the carboxylic acid from the site of a specific ring C

Table 2. *Short intermolecular* Cl···Cl' *distances* (Å) *and angles* (°)

Compound	Distance Cl···Cl'	Angle C—Cl···Cl'	Reference
Tetrachlorohydroquinone	3·37	168 and 168	Sakurai (1962)
2,5-Dichloroaniline	3·37	157 and 166	Sakurai *et al.* (1963)
Dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (yellow form)	3·47	147 and 147	Byrn, Curtin & Paul (1971)
4-Chlorobenzoic acid	3·44	167 and 167	Miller, Paul & Curtin (1974)
1,4-Dichlorobenzene (β form)	3·38	169·5 and 169·5	Wheeler & Colson (1975)
N-(n-Butyl)-N'-[(4-chlorophenoxy)acetyl]urea	3·361 (4)	147·9 (5) and 147·9 (5)	Vijay Kumar & Rao (1982a)
(4-Chlorophenoxy)acetic acid	3·349 (3)	177·1 (3) and 177·1 (3)	Present work

atom having an induced fractional positive charge. The equivalent distance [O(3)···C(5)] in this molecule was found to be 5·042 (2) Å which is closest to the postulated distance of 5·50 Å, whereas the corresponding distances in other substituted phenoxyacetic acids are 4·20 in (2,4-dichlorophenoxy)acetic acid (Smith, Kennard & White, 1976a), 4·29 in (2,4,5-trichlorophenoxy)acetic acid (Smith, Kennard & White, 1976b), 4·17 in (2,5-dichlorophenoxy)acetic acid (Smith, Whitnall & Kennard, 1976) and 4·28 Å in (2,4,6-trichlorophenoxy)acetic acid (Smith, Kennard & White, 1977).

The C(1)—Cl bond is symmetrical in the plane of the benzene ring. The planar acetic acid group makes an angle of 3·2 (3)° with the plane of the ring, which compares well with 5·5 (3) in (4-nitrophenoxy)acetic acid (Vijay Kumar & Rao, 1980), 4·15 in (2,4,5-trichlorophenoxy)acetic acid (Smith, Kennard & White, 1976b) and 7·9 (2)° in (4-methylphenoxy)acetic acid (Vijay Kumar & Rao, 1982b).

A short intermolecular Cl···Cl' distance 3·349 (3) Å was observed. The angle C(1)—Cl···Cl' of 177·1 (3)° is slightly different from the orientation factor condition (Sakurai, Sundaralingam & Jeffrey, 1963). Table 2 gives a list of some Cl···Cl' short intermolecular distances. The molecules are stacked in layers parallel to the (010) plane.

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