

difference map showed low peaks ( $\sim 0.5 \text{ e } \text{\AA}^{-3}$ ) close to Cl(1), as well as the higher peak near Cl(2) noted in the experimental section. This indicates some freedom of rotation about the C(2)–C(3) bond.

The C–C bond lengths in the cyclopropane ring follow the trend noted for attached electron-acceptor groups (Allen, 1980). The bond between the carbon atoms to which such groups are attached [C(3)–C(7)] is longer [1.548 (6) Å] than the other two [1.503 (6) and 1.527 (6) Å]. The latter are not as equal as would have been expected by more strict adherence to the additivity rule.

Other bond lengths and angles are similar to those found in other pyrethroids (Owen, 1976, and references therein).

The torsion angles and mean planes, however, show how flexible these molecules are. Thus the plane of the dichlorovinyl group does not bisect C(4)–C(7), though the torsion about C(2)–C(3) is not as extreme as that found in deltamethrin itself (Owen, 1975). The ester group also deviates slightly from the bisecting position, to a greater extent than found in other pyrethroids. The torsions around the other bonds about which free rotation may be expected are completely different from those in similar molecules, and bring the terminal benzene ring round towards the dichlorovinyl group, rather than towards the dimethyl group as found in NRDC 157 (Owen, 1976).

There are no close intermolecular contacts of note, so the conformation is not determined by strong interactions between the molecules, such as stacking of benzene rings, *etc.* Left- and right-handed forms of the molecule, ( $\alpha S$ ), (1*S*,*trans*) and ( $\alpha R$ ), (1*R*,*trans*), are present in equal numbers, giving the racemic crystals.

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### (±)-2-(4-Chlorophenoxy)-2-phenylpropionic Acid

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**Abstract.** C<sub>15</sub>H<sub>13</sub>ClO<sub>3</sub>, m.p. 379–381 K,  $M_r = 276.7$ , monoclinic,  $P2_1/c$ ,  $a = 15.328$  (8),  $b = 6.079$  (5),  $c = 16.398$  (7) Å,  $\beta = 113.79$  (3)°,  $Z = 4$ ,  $D_x = 1.314$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.278$  mm<sup>-1</sup>,  $R = 0.086$ , 918 observed reflexions. The molecules, which form hydrogen-bonded cyclic dimers [O...O, 2.638 (9) Å], adopt a conformation with the phenoxy and benzene rings

nearly coplanar. The carboxylic acid group has the *syn-anti* conformational motif relative to the phenoxy residue, common to all known phenoxyalkanoic acids having tertiary substitution about the  $\alpha$ -carbon.

**Introduction.** The title compound is an experimental anti-hypolipidaemic compound from the Merck Com-

pany, Darmstadt (compound EMD 30702) (Schacht, 1977). Although a member of the phenoxyalkanoic acid series of which a number of the acetic and 2-propionic acid derivatives have herbicidal properties, this compound has negligible auxin properties. The structures of four other similar hypocholesteraeamic 2-methylpropionic acids [2-methyl-2-phenoxypropionic acid, 2-(4-chlorophenoxy)-2-methylpropionic acid (clofibric acid) (Kennard, Smith & White, 1981), 2-(4-dibenzofuranyloxy)-2-methylpropionic acid (Wagner & Malmros, 1979a) and 2-[2-(phenoxy)phenoxy]-2-methylpropionic acid (Wagner & Malmros, 1979b)] are now known. The structure was determined to provide precise structural information about this group of compounds and to observe the effect of the presence of the second phenyl ring on the overall molecular conformation of the phenoxyalkanoic acid residue.

Crystals suitable for X-ray analysis were obtained from cyclohexane. 918 reflexions with  $I > 1.25\sigma(I)$  were considered observed out of 1141 in a unique set

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	$B_{eq}$ (Å <sup>2</sup> )
Cl(4)	4547 (2)	3360 (6)	9043 (2)	9.4 (2)
O(7)	2804 (3)	5046 (9)	5183 (4)	4.7 (4)
O(10)	567 (3)	7294 (8)	4898 (3)	4.8 (4)
O(11)	1068 (4)	3791 (8)	5033 (3)	5.1 (4)
C(1)	3168 (6)	4764 (15)	6094 (6)	4.2 (7)
C(2)	3878 (6)	3195 (15)	6414 (6)	5.0 (7)
C(3)	4303 (7)	2752 (16)	7329 (8)	6.1 (8)
C(4)	4011 (8)	3907 (21)	7897 (6)	5.9 (8)
C(5)	3314 (7)	5455 (19)	7605 (7)	6.1 (8)
C(6)	2873 (6)	5879 (16)	6683 (7)	5.7 (7)
C(8)	2042 (5)	6560 (13)	4740 (5)	4.5 (6)
C(9)	1154 (5)	5869 (13)	4919 (4)	5.3 (7)
C(81)	2380 (6)	8946 (13)	4982 (6)	3.9 (5)
C(11)	1716 (6)	6143 (15)	3738 (6)	4.0 (6)
C(12)	2062 (6)	4398 (15)	3418 (6)	5.7 (7)
C(13)	1721 (8)	4092 (17)	2485 (8)	7.6 (8)
C(14)	1056 (7)	5444 (19)	1877 (7)	6.2 (8)
C(15)	754 (6)	7191 (19)	2247 (8)	6.7 (8)
C(16)	1072 (7)	7583 (16)	3162 (7)	5.7 (7)
H(2)	4213	2315	5977	
H(3)	4721	891	7384	
H(5)	2839	6154	7964	
H(6)	2232	7029	6426	
H(11)	*			
H(12)	2569	3175	3849	
H(13)	2167	3261	2187	
H(14)	*			
H(15)	59	8112	1721	
H(16)	*			
H(811)	2538	9723	5647	
H(812)	1836	10303	4595	
H(813)	*			

\* Not located.

collected from one crystal (0.18 × 0.30 × 0.10 mm) mounted about the *b* (prism) axis on a Syntex P2<sub>1</sub> four-circle diffractometer ( $2\theta_{max} < 50^\circ$ , graphite-monochromated Mo  $K\alpha$  radiation). No corrections were made for absorption [ $\mu(\text{Mo } K\alpha) = 0.278 \text{ mm}^{-1}$ ].

The structure was solved by multiresolution  $\sum_2$  sign expansion (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic temperature factors for all non-H atoms reduced  $R[\sum ||F_o| - |F_c|| / \sum F_o]$  from an initial value of 0.31 to 0.086 and  $R_w[\sum w||F_o| - |F_c||^2 / \sum w(F_o)^2]$  to 0.081 [ $w = 1.82/\sigma^2(F_o) + 5.4 \times 10^{-4}(F_o)^2$ ]. Most 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 Å<sup>2</sup>. Two intense low-angle reflections (011, 200) were considered to be seriously affected by extinction and were removed before the final cycle of refinement. A final difference-electron-density synthesis revealed no features greater than 0.141 e Å<sup>-3</sup>. The high residual *R* is considered to be a consequence of the high thermal motion for a number of atoms in the molecule. 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 listed in Table 2.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35917 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses

C(1)–C(2)	1.382 (12)	C(8)–C(81)	1.537 (11)
C(2)–C(3)	1.401 (15)	C(8)–C(11)	1.534 (12)
C(3)–C(4)	1.377 (18)	C(9)–O(10)	1.239 (9)
C(4)–Cl(4)	1.752 (10)	C(9)–O(11)	1.291 (9)
C(4)–C(5)	1.358 (16)	C(11)–C(12)	1.380 (14)
C(5)–C(6)	1.409 (14)	C(12)–C(13)	1.417 (16)
C(6)–C(1)	1.395 (16)	C(13)–C(14)	1.374 (14)
C(1)–O(7)	1.379 (11)	C(14)–C(15)	1.391 (17)
O(7)–C(8)	1.434 (9)	C(15)–C(16)	1.398 (16)
C(8)–C(9)	1.561 (12)	C(16)–C(11)	1.371 (12)
C(1)–C(2)–C(3)	119.6 (10)	C(9)–C(8)–C(11)	103.0 (6)
C(2)–C(3)–C(4)	119.3 (9)	C(8)–C(11)–C(12)	121.6 (7)
C(3)–C(4)–C(5)	122.6 (9)	C(8)–C(11)–C(16)	117.7 (9)
C(3)–C(4)–Cl(4)	119.3 (8)	C(11)–C(12)–C(13)	118.7 (8)
C(5)–C(4)–Cl(4)	118.2 (9)	C(12)–C(13)–C(14)	123.2 (12)
C(4)–C(5)–C(6)	118.4 (11)	C(13)–C(14)–C(15)	114.9 (10)
C(5)–C(6)–C(1)	120.2 (9)	C(14)–C(15)–C(16)	124.3 (9)
C(6)–C(1)–C(2)	119.9 (9)	C(15)–C(16)–C(11)	118.2 (10)
C(6)–C(1)–O(7)	125.9 (7)	C(16)–C(11)–C(12)	120.6 (9)
C(2)–C(1)–O(7)	114.1 (9)	C(8)–C(9)–O(10)	119.0 (7)
C(1)–O(7)–C(8)	121.3 (7)	C(8)–C(9)–O(11)	116.0 (7)
O(7)–C(8)–C(9)	109.0 (6)	O(10)–C(9)–O(11)	125.0 (8)
O(7)–C(8)–C(81)	110.8 (5)		
O(7)–C(8)–C(11)	106.5 (7)		
C(81)–C(8)–C(9)	115.7 (8)		
C(81)–C(8)–C(11)	111.3 (7)		

**Discussion.** The title compound (EMD 30702) forms the usual centrosymmetric hydrogen-bonded cyclic dimers [O...O, 2.638 (9) Å]. The conformation adopted is such that the planes of the 2-phenyl group and the 4-chlorophenoxy group are nearly coplanar [the dihedral angle between the least-squares planes to these groups is 12.8 (5)°]. The carboxylic acid group is orientated almost perpendicular to these planes (Fig. 1). This is similar to that found for bis(4-chlorophenoxy)acetic acid (Smith & Kennard, 1981) and bis(4-chlorophenyl)acetic acid (Shields & Kennard, 1977; Hovmöller, Norrestam & Palm, 1977). The major chemical difference is the presence of an  $\alpha$ -methyl group in the title compound. The gross conformation of the oxypropionic acid residue for the known phenoxy acids is such that one  $\alpha$ -methyl group lies approximately in the plane of the phenoxy group. In EMD 30702, it

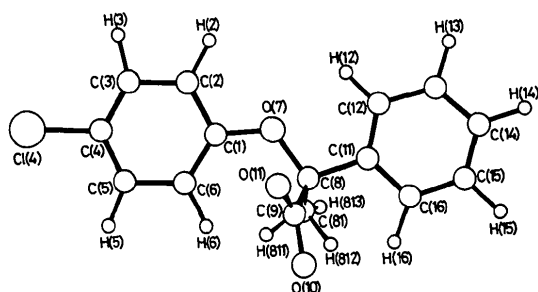


Fig. 1. Molecular conformation and atom-naming scheme in a view perpendicular to the plane of C(1), O(7), C(8). Hydrogen atoms H(14), H(16) and H(813) are included at their calculated positions.

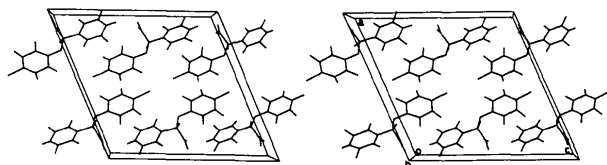


Fig. 2. Stereoscopic view of the packing in the cell perpendicular to the *ac* plane.

Table 3. Torsion angles ( $^{\circ}$ ) within the oxypropionic acid side chain compared with those for 2-phenoxy-2-methylpropionic acid (PMP) and 2-(4-chlorophenoxy)-2-methylpropionic acid (CPMP) (Kennard *et al.*, 1981)

		PMP	CPMP
C(2)—C(1)—O(7)—C(8)	+178.9 (6)	+167.8 (3)	+130.3 (4)
C(1)—O(7)—C(8)—C(9)	-60.0 (6)	-61.6 (3)	-79.0 (4)
C(1)—O(7)—C(8)—C(81)	+68.4 (6)	+65.6 (3)	+47.2 (4)
C(1)—O(7)—C(8)—C(11)	-170.5 (6)	+178.5 (3)	+167.8 (4)
O(7)—C(8)—C(9)—O(10)	+153.3 (6)	-155.6 (3)	+147.0 (4)
O(7)—C(8)—C(11)—C(16)	-171.7 (6)	-	-

appears that packing effects favour the situation where the two ring systems are coplanar while the single  $\alpha$ -methyl group [C(81)] lies below the plane (Fig. 2). This group in turn stabilizes the position of the carboxylic acid group with relatively close contacts [O(10)—H(811), O(11)—H(812)] of 3.13 and 2.66 Å respectively. The torsion angles about vectors in the side chain are listed in Table 3 and are compared with 2-phenoxy-2-methylpropionic acid (PMP) and 2-(4-chlorophenoxy)-2-methylpropionic acid (CPMP) (Kennard *et al.*, 1981). The resemblance is greater to PMP with the side chain being perturbed by intramolecular interactions in CPMP.

Although the carboxyl proton was not located, the O atoms are identified as carbonyl [O(10)] and hydroxyl [O(11)] on the basis of the C—C—O angles [C(8)—C(9)—O(10), 119.0 (7); C(8)—C(9)—O(11), 116.0 (7)°]. This places O(11) 2.681 (9) Å from the ether oxygen O(7) compared to the two O...O interactive distances of 2.730 (8) and 2.891 (8) Å for bis(4-chlorophenoxy)acetic acid. The mean for this distance over a series of phenoxyalkanoic acids is 2.711 Å. The conformational motif for the acid group is therefore synclinal-anticlinal (carbonyl). This has been found for all the known 2-aryloxypropionic acids with tertiary substitutions at the  $\alpha$ -carbon. They are PMP, CPMP, 2-(4-dibenzofuranyloxy)-2-methylpropionic acid (Wagner & Malmros, 1979a) and 2-[2-(phenoxy)phenoxy]-2-methylpropionic acid (Wagner & Malmros, 1979b).

Distortion of the *exo*-C(1) ring angles in the phenoxy group is also present in this example [C(2)—C(1)—O(7), 114.1 (9), and C(6)—C(1)—O(7), 125.9 (7)°].

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## (4-Chlorophenoxy)acetic Acid

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**Abstract.**  $C_8H_7ClO_3$ , 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)°,  $V = 404.6$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.53$  Mg m<sup>-3</sup>,  $\mu(Mo K\alpha) = 0.435$  mm<sup>-1</sup>,  $R = 0.048$ , 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 ( $2\theta_{\max} = 50^\circ$ ,  $Mo K\alpha$ ) (graphite monochromator). No corrections were made for absorption [ $\mu(Mo K\alpha) = 0.435$  mm<sup>-1</sup>]. 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 Å<sup>2</sup>. Three intense low-angle reflexions (111,  $\bar{1}20$ ,  $2\bar{1}1$ ) were