

Structural Aspects of Phenoxyalkanoic Acids.

X. Bis(2-chlorophenoxy)acetic Acid and Bis(4-chlorophenoxy)acetic Acid

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Abstract

The crystal structures of two isomeric bis(phenoxy) acids [bis(2-chlorophenoxy)acetic acid (I) and bis(4-chlorophenoxy)acetic acid (II)] have been determined by direct methods using three-dimensional X-ray diffractometer data. Both are triclinic, space group $P\bar{1}$ with $Z = 2$. (I), $C_{14}H_{10}Cl_2O_4$, $M_r = 313.1$, has $a = 11.163$ (1), $b = 9.061$ (1), $c = 7.298$ (1) Å, $\alpha = 80.659$ (9), $\beta = 99.683$ (9), $\gamma = 105.218$ (5)°, $V = 696.8$ Å³, $F(000) = 320$, $D_x = 1.49$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.477$ mm⁻¹. (II), $C_{14}H_{10}Cl_2O_4$, $M_r = 313.1$, has $a = 14.661$ (4), $b = 10.261$ (2), $c = 4.708$ (1) Å, $\alpha = 94.10$ (3), $\beta = 87.44$ (2), $\gamma = 80.45$ (2)°, $V = 695.5$ Å³, $F(000) = 320$, $D_x = 1.49$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.478$ mm⁻¹. (I) and (II) were refined to $R = 0.049$ and 0.086 for 1138 and 1081 independent observed reflections respectively. Both (I) and (II) form the usual hydrogen-bonded cyclic dimers *via* the carboxylic acid groups with O...O distances of 2.662 (5) (I) and 2.663 (10) Å (II). Conformationally, however, the two isomers are substantially different. In (I) the two phenoxy rings have a pseudo twofold rotational relationship with the 2-chloro substituents mutually *trans*. The parallel orientation of the carboxyl group gives two independent O...O interactions [2.746, 2.646 (6) Å] involving both ether and both carboxyl oxygens. In (II), the rings are more regularly disposed towards the carboxylic acid group, the ring-to-ring and ring-to-carboxylic acid dihedral angles being 59.7, 48.3 and 44.9 (9)° respectively. This conformation with the carboxylic acid group oriented approximately perpendicular to the line through the ether oxygens results in two similar close intramolecular O(carboxyl)–O(ether) contacts [2.730, 2.891 (8) Å] in a bifurcated mode involving one carboxyl oxygen only.

Introduction

The title compounds bis(2-chlorophenoxy)acetic acid (I) and bis(4-chlorophenoxy)acetic acid (II) are isomeric members of a series of synthetic auxin compounds of the phenoxyalkanoic acid series, the structural systematics of a number of which have already been described (Smith & Kennard, 1979; Kennard, Smith & White, 1981*a*). The preparation of bis(2-chlorophenoxy)acetic acid was first reported by (Synerholm & Zimmerman, 1945) and, unlike its monophenoxy analogue (2-chlorophenoxy)acetic acid, (I) is herbicidally inactive. X-ray structure determinations of (2-chlorophenoxy)acetic acid (Chandrasekhar & Pattabhi, 1977; Kennard & Smith, 1981), (4-chlorophenoxy)acetic acid (Kennard, Smith & White, 1981*b*) and the majority of phenoxyacetic acids and phenoxyacetic acid complexes (Smith, O'Reilly, Kennard, Stadnicka & Oléksyn, 1981; Smith, O'Reilly & Kennard, 1980) indicate that the preferred solid-state conformation is one with the benzene ring and the carboxylic acid group coplanar.

The structures of these two isomers were determined to compare the effect of the presence of different ring-chlorine substitution on the molecular conformation and to provide precise data for use in correlation studies on this series of compounds.

Experimental

Both compounds were prepared by the reaction of stoichiometric amounts of dichloroacetic acid and sodium 2-chlorophenoxide (I) and sodium 4-chlorophenoxide (II) (Synerholm & Zimmerman, 1945). Colourless crystals were obtained from benzene. Crystals used for data collection measured $0.18 \times 0.12 \times 0.30$ and $0.23 \times 0.10 \times 0.35$ mm for (I) and (II) respectively. The data were collected on an automated

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Hilger & Watts four-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation. Accurate cell dimensions for both compounds were obtained by least-squares refinement of angle data from 12 accurately centred reflections. 1138 (I) and 1081 (II) reflections with $I > 2.5\sigma(I)$ were considered observed out of 1540 (I) and 1514 (II) collected in a limiting sphere up to $2\theta_{\max} = 50^\circ$. The data were corrected for Lorentz and polarization effects, but not for absorption [$\mu(\text{Mo } K\alpha) = 0.48 \text{ mm}^{-1}$].

Both structures were solved by multiresolution \sum_2 sign expansion (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms reduced $R[\sum |F_o| - |F_c|] / \sum |F_o|$ to 0.049 (I) and 0.086 (II) and $R_w[\sum w|F_o| - |F_c|] / \sum wF_o^2$ to 0.049 (I) and 0.088 (II). The value of w used in the weighting scheme was $2.07/(\sigma^2 F_o + 3.88 \times 10^{-4} F_o^2)$ (I) and $3.1/(\sigma^2 F_o + 9.9 \times 10^{-4} F_o^2)$ (II). Most H positions were located in difference Fourier syntheses and included in the

refinement at fixed positions with the values of their isotropic thermal parameters (U) fixed at 0.05 \AA^2 . Final difference Fourier syntheses revealed no features greater than 0.094 and 0.145 e \AA^{-3} for (I) and (II) respectively. For (I), two intense low-angle reflections (100, 210) were considered to be affected by extinction and removed before the final cycle of refinement. No such effects were in evidence in (II). Atomic scattering factors were those of Cromer & Mann (1968) for non-H atoms and Stewart, Davidson & Simpson (1965) for H. Positional parameters are listed in Table 1* while bond distances and angles are given in Tables 2 and 3. The molecular conformations and atom-numbering schemes are shown in Figs. 1 and 2.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36107 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters ($\times 10^4$) with equivalent isotropic thermal parameters ($\times 10^3$) for (I) and (II), with e.s.d.'s in parentheses

B_{eq} is defined as $(B_{11} \times B_{22} \times B_{33})^{1/3}$.

	x	y	z	B_{eq} (\AA^2)		x	y	z	B_{eq} (\AA^2)
(I) Bis(2-chlorophenoxy)acetic acid					(II) Bis(4-chlorophenoxy)acetic acid				
Cl(21)	7921 (2)	323 (2)		6.5 (1)	Cl(41)	-764 (2)	-3081 (4)	1824 (9)	10.4 (3)
Cl(22)	7770 (2)	6132 (2)	-3050 (2)	4.8 (1)	Cl(42)	2786 (2)	3975 (2)	4158 (7)	6.7 (2)
O(71)	6542 (3)	2497 (4)	2189 (4)	3.2 (2)	O(71)	2716	-2060 (5)	-3547 (13)	4.9 (4)
O(72)	6582 (3)	4812 (4)	209 (4)	2.6 (2)	O(72)	3976 (4)	-1133 (5)	-2488 (12)	4.6 (4)
O(10)	5643 (3)	5661 (4)	3015 (5)	3.3 (2)	O(10)	4370 (4)	-4388 (5)	-2087 (14)	5.3 (5)
O(11)	5231 (3)	3249 (4)	4440 (5)	4.0 (2)	O(11)	4497 (5)	-3382 (6)	-6039 (14)	6.8 (5)
C(11)	6640 (5)	1532 (6)	980 (7)	2.8 (3)	C(11)	1911 (7)	-2331 (9)	-2110 (23)	4.8 (7)
C(21)	7278 (5)	411 (6)	1748 (7)	3.5 (4)	C(21)	1102 (7)	-1486 (10)	-2738 (25)	6.8 (8)
C(31)	7416 (6)	-641 (7)	659 (9)	4.4 (4)	C(31)	297 (7)	-1748 (10)	-1531 (27)	7.1 (9)
C(41)	6925 (6)	-568 (7)	-1188 (9)	4.3 (4)	C(41)	285 (7)	-2758 (11)	173 (25)	6.6 (8)
C(51)	6301 (5)	550 (6)	-1984 (7)	3.8 (4)	C(51)	1082 (8)	-3550 (9)	795 (24)	5.8 (8)
C(61)	6146 (5)	1596 (6)	-903 (7)	3.6 (3)	C(61)	1913 (6)	-3333 (9)	-457 (25)	5.4 (8)
C(12)	7839 (4)	5477 (5)	717 (7)	2.6 (3)	C(12)	3645 (5)	44 (8)	-900 (20)	4.0 (6)
C(22)	8502 (5)	6203 (6)	-764 (7)	3.4 (3)	C(22)	4080 (6)	1092 (9)	-1456 (20)	4.7 (7)
C(32)	9743 (6)	7008 (7)	-444 (9)	4.5 (4)	C(32)	3796 (7)	2307 (8)	97 (23)	5.2 (6)
C(42)	10316 (6)	7069 (8)	1374 (10)	4.9 (4)	C(42)	3106 (6)	2438 (8)	2217 (21)	4.4 (7)
C(52)	9678 (5)	6339 (7)	2883 (8)	4.1 (4)	C(52)	2683 (6)	1414 (9)	2864 (22)	5.5 (6)
C(62)	8438 (5)	5515 (6)	2535 (7)	3.2 (3)	C(62)	2939 (6)	184 (8)	1223 (21)	4.8 (6)
C(8)	5913 (5)	3667 (6)	1448 (7)	2.9 (3)	C(8)	3536 (5)	-2229 (7)	-2042 (18)	3.8 (5)
C(9)	5599 (4)	4296 (6)	3085 (6)	2.8 (3)	C(9)	4189 (5)	-3443 (7)	-3453 (19)	4.3 (5)
H(31)	8101	-1213	1323		H(21)	*			
H(41)	6997	-1379	-2124		H(31)	-282	-1049	-1554	
H(51)	5788	645	-3311		H(51)	1230	-4443	2127	
H(61)	5724	2473	-1582		H(61)	2470	-4001	-15	
H(32)	10192	7740	-1779		H(32)	4457	1065	-3209	
H(42)	11286	7651	1634		H(42)	4164	3177	-543	
H(52)	*				H(52)	2334	1266	1900	
H(62)	7926	4902	3642		H(62)	2643	-707	1632	
H(8)	5025	3240	670		H(8)	3366	-2277	551	
H(11)	*				H(11)	*			

* Not located.

Table 2. *Interatomic distances (Å) and angles (°) for (I) compared with those for (±)-2-(2-chlorophenoxy)propionic acid (OCPPA) (Smith, Kennard & White, 1981)*

E.s.d.'s are given in parentheses.

(a) Distances		(b) Angles		OCPPA		Residue 1		Residue 2		OCPPA		Residue 2		OCPPA	
C(11)–C(21)	1.383 (8)	C(11)–C(21)–C(31)	120.6 (5)	C(12)–C(22)	1.385 (3)	C(11)–C(21)–C(31)	120.6 (5)	C(12)–C(22)–C(32)	121.0 (5)	C(12)–C(22)–C(32)	120.3 (2)	C(12)–C(22)–C(32)	121.0 (5)	C(12)–C(22)–C(32)	120.3 (2)
C(21)–C(31)	1.389 (10)	C(11)–C(21)–C(21)	119.8 (5)	C(22)–C(32)	1.394 (3)	C(21)–C(31)–C(41)	119.9 (6)	C(22)–C(32)	120.0 (4)	C(21)–C(31)–C(41)	119.7 (2)	C(22)–C(32)	120.0 (4)	C(21)–C(31)–C(41)	119.7 (2)
C(21)–C(21)	1.737 (5)	C(21)–C(31)–C(41)	119.9 (6)	C(22)–C(42)	1.736 (2)	C(31)–C(41)–C(51)	120.4 (6)	C(22)–C(42)	118.8 (6)	C(32)–C(42)–C(52)	120.3 (2)	C(22)–C(42)	118.8 (6)	C(32)–C(42)–C(52)	120.3 (2)
C(31)–C(41)	1.365 (9)	C(31)–C(41)–C(51)	119.6 (5)	C(32)–C(42)	1.365 (3)	C(31)–C(41)–C(21)	120.1 (5)	C(32)–C(42)	121.5 (5)	C(32)–C(42)–C(52)	120.1 (2)	C(32)–C(42)–C(52)	121.5 (5)	C(32)–C(42)–C(52)	120.1 (2)
C(41)–C(51)	1.376 (9)	C(41)–C(51)–C(61)	120.1 (5)	C(42)–C(52)	1.377 (3)	C(41)–C(51)–C(61)	120.1 (5)	C(42)–C(52)	119.1 (4)	C(42)–C(52)–C(62)	120.1 (2)	C(42)–C(52)–C(62)	119.1 (4)	C(42)–C(52)–C(62)	120.1 (2)
C(51)–C(61)	1.387 (9)	C(51)–C(61)–C(11)	120.0 (5)	C(52)–C(62)	1.399 (3)	C(51)–C(61)–C(11)	120.0 (5)	C(52)–C(62)	120.2 (5)	C(52)–C(62)–C(12)	120.0 (2)	C(52)–C(62)–C(12)	120.2 (5)	C(52)–C(62)–C(12)	120.0 (2)
C(61)–C(11)	1.390 (7)	C(61)–C(11)–C(21)	119.0 (5)	C(62)–C(12)	1.386 (3)	C(61)–C(11)–C(21)	119.0 (5)	C(62)–C(12)	119.5 (4)	C(62)–C(12)–C(22)	119.2 (2)	C(62)–C(12)–C(22)	119.5 (4)	C(62)–C(12)–C(22)	119.2 (2)
C(11)–O(71)	1.374 (7)	C(61)–C(11)–O(71)	125.3 (5)	C(12)–O(72)	1.371 (2)	C(61)–C(11)–O(71)	115.8 (4)	C(12)–O(72)	125.3 (4)	C(62)–C(12)–O(72)	125.3 (4)	C(62)–C(12)–O(72)	125.3 (4)	C(62)–C(12)–O(72)	125.0 (2)
O(71)–C(8)	1.409 (6)	C(21)–C(11)–O(71)	117.3 (4)	O(72)–C(8)	1.424 (2)	C(21)–C(11)–O(71)	108.1 (4)	O(72)–C(8)	120.2 (3)	O(72)–C(8)–C(9)	113.4 (4)	O(72)–C(8)–C(9)	113.4 (4)	O(72)–C(8)–C(9)	106.1 (2)
C(8)–C(9)	1.530 (6)	C(8)–C(9)–O(10)	120.8 (4)	C(8)–C(9)	1.514 (3)	C(8)–C(9)–O(10)	120.8 (4)	C(8)–C(9)	123.2 (2)	C(8)–C(9)–O(10)	123.2 (2)	C(8)–C(9)	123.2 (2)	C(8)–C(9)	123.2 (2)
C(9)–O(10)	1.218 (6)	C(8)–C(9)–O(11)	114.1 (4)	C(9)–O(10)	1.214 (2)	C(8)–C(9)–O(11)	114.1 (4)	C(9)–O(10)	112.3 (2)	C(9)–O(10)	112.3 (2)	C(9)–O(10)	112.3 (2)	C(9)–O(10)	112.3 (2)
O(9)–O(11)	1.294 (6)	O(10)–C(9)–O(11)	125.0 (5)	O(9)–O(11)	1.306 (2)	O(10)–C(9)–O(11)	125.0 (5)	O(9)–O(11)	124.4 (4)	O(10)–C(9)–O(11)	124.4 (4)	O(9)–O(11)	124.4 (4)	O(10)–C(9)–O(11)	124.4 (4)
O(10)···O(11) ^y	2.662 (5)														

Table 3. *Interatomic distances (Å) and angles (°) for (II) compared with those for (±)-2-(4-chlorophenoxy)propionic acid (PCPPA) (Kennard, Smith & White, 1981a)*

E.s.d.'s are given in parentheses.

(a) Distances		(b) Angles		PCPPA		Residue 1		Residue 2		PCPPA		Residue 2		PCPPA	
C(11)–C(21)	1.405 (13)	C(11)–C(21)–C(31)	115.6 (10)	C(12)–C(22)	1.390 (8)	C(11)–C(21)–C(31)	115.6 (10)	C(12)–C(22)	119.3 (8)	C(12)–C(22)–C(32)	120.7 (6)	C(12)–C(22)–C(32)	119.3 (8)	C(12)–C(22)–C(32)	120.7 (6)
C(21)–C(31)	1.363 (15)	C(21)–C(31)–C(41)	121.8 (10)	C(22)–C(32)	1.383 (9)	C(21)–C(31)–C(41)	121.8 (10)	C(22)–C(32)	120.0 (9)	C(22)–C(32)–C(42)	118.8 (6)	C(22)–C(32)–C(42)	120.0 (9)	C(22)–C(32)–C(42)	118.8 (6)
C(31)–C(41)	1.357 (17)	C(31)–C(41)–C(51)	121.5 (10)	C(32)–C(42)	1.389 (8)	C(31)–C(41)–C(51)	121.5 (10)	C(32)–C(42)	122.0 (8)	C(32)–C(42)–C(52)	121.7 (6)	C(32)–C(42)–C(52)	122.0 (8)	C(32)–C(42)–C(52)	121.7 (6)
C(41)–C(51)	1.782 (12)	C(41)–C(51)–C(61)	118.2 (9)	C(42)–C(52)	1.746 (6)	C(41)–C(51)–C(61)	118.2 (9)	C(42)–C(52)	118.4 (7)	C(42)–C(52)–C(62)	119.1 (5)	C(42)–C(52)–C(62)	118.4 (7)	C(42)–C(52)–C(62)	119.1 (5)
C(51)–C(61)	1.365 (15)	C(51)–C(61)–C(11)	116.5 (9)	C(42)–C(52)	1.384 (9)	C(41)–C(51)–C(61)	118.2 (9)	C(42)–C(52)	118.7 (7)	C(42)–C(52)–C(62)	119.4 (6)	C(42)–C(52)–C(62)	118.7 (7)	C(42)–C(52)–C(62)	119.4 (6)
C(61)–C(11)	1.387 (15)	C(61)–C(11)–O(71)	123.5 (10)	C(52)–C(62)	1.393 (9)	C(51)–C(61)–C(11)	116.5 (9)	C(52)–C(62)	119.6 (7)	C(52)–C(62)–C(12)	119.2 (5)	C(52)–C(62)–C(12)	119.6 (7)	C(52)–C(62)–C(12)	119.2 (5)
C(11)–O(71)	1.412 (12)	C(61)–C(11)–O(71)	119.4 (9)	C(62)–C(12)	1.402 (8)	C(61)–C(11)–O(71)	119.4 (9)	C(62)–C(12)	120.6 (7)	C(62)–C(12)–C(22)	120.1 (6)	C(62)–C(12)–C(22)	120.6 (7)	C(62)–C(12)–C(22)	120.1 (6)
O(71)–C(8)	1.414 (10)	C(21)–C(11)–O(71)	123.4 (8)	C(12)–O(72)	1.365 (7)	C(21)–C(11)–O(71)	123.4 (8)	C(12)–O(72)	123.4 (8)	C(22)–C(12)–O(72)	123.4 (8)	C(22)–C(12)–O(72)	123.4 (8)	C(22)–C(12)–O(72)	123.4 (8)
C(8)–C(9)	1.530 (10)	C(11)–O(71)–C(8)	116.5 (7)	O(72)–C(8)	1.434 (7)	C(11)–O(71)–C(8)	116.5 (7)	O(72)–C(8)	118.0 (6)	O(72)–C(8)–C(9)	105.9 (6)	O(72)–C(8)–C(9)	105.9 (6)	O(72)–C(8)–C(9)	105.9 (6)
C(9)–O(10)	1.202 (11)	O(71)–C(8)–O(72)	107.1 (6)	C(8)–C(9)	1.535 (8)	O(71)–C(8)–O(72)	107.1 (6)	C(8)–C(9)	123.5 (6)	C(8)–C(9)–O(10)	123.5 (6)	C(8)–C(9)	123.5 (6)	C(8)–C(9)–O(10)	123.5 (6)
C(9)–O(11)	1.289 (11)	C(8)–C(9)–O(10)	117.8 (8)	C(9)–O(10)	1.215 (8)	C(8)–C(9)–O(10)	117.8 (8)	C(9)–O(10)	117.4 (7)	C(9)–O(10)	117.4 (7)	C(9)–O(10)	117.4 (7)	C(9)–O(10)	117.4 (7)
O(10)···O(11) ^y	2.663 (10)	O(10)–C(9)–O(11)	124.7 (7)	O(10)–C(9)–O(11)	1.296 (7)	O(10)–C(9)–O(11)	124.7 (7)	O(10)–C(9)–O(11)	124.7 (7)	O(10)–C(9)–O(11)	124.7 (7)	O(10)–C(9)–O(11)	124.7 (7)	O(10)–C(9)–O(11)	124.7 (7)

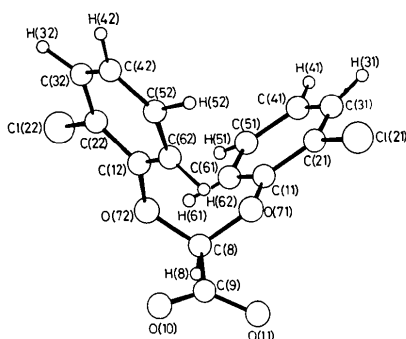


Fig. 1. Molecular conformation and atom-naming scheme for bis(2-chlorophenoxy)acetic acid (I).

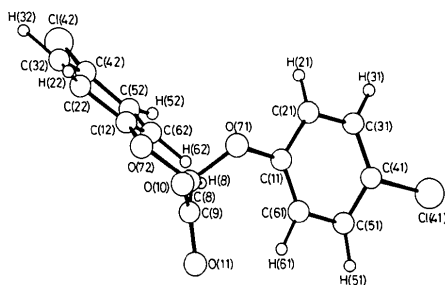


Fig. 2. Molecular conformation and atom-naming scheme for bis(4-chlorophenoxy)acetic acid (II).

Discussion

The molecules of (I) and (II) form hydrogen-bonded cyclic dimers [O...O, 2.662 (5) (I); 2.663 (10) Å (II)], common to members of the mono-phenoxyalkanoic acid series (Kennard, Smith & White, 1981a). Interatomic distances and angles are also similar to those for the same series of acids, including the distortion of the *exo* C(11) and C(12) ring angles [125.3 (5), 115.8 (4)° and 125.3 (4), 115.1 (4)° for (I) and 123.4 (8), 113.0 (9)° and 123.4 (8), 115.9 (7)° for (II)]. The angular distortion about the carboxylic acid group, another feature of all known phenoxy acids, is also in evidence in (I). In this case the C—C—O angles [120.8, 114.1 (4)°] are considered normal for non-disordered carboxylic acid structures (Leiserowitz, 1976). Although the acid proton was not located, assignment is possible on the basis of the C=C=O and C—C—O(H) angles and the C—O bond distances [1.218 (6), 1.294 (6) Å]. This places the carbonyl oxygen [O(10)] 2.646 (6) Å from the ether oxygen [O(72)] of one phenoxy residue while O(11) is at a similar interactive distance [2.746 (6) Å] from the ether oxygen [O(71)] of the second phenoxy residue. These distances are within the range of 2.5–2.7 Å found for the series of mono-acids irrespective of the conformation of the acid. This means that the plane of the carboxylic acid group lies approximately parallel to the line through the ether oxygens, making dihedral angles

of 47.7 (9) and 74.4 (9)° with the planes of the benzene rings. The benzene ring-to-ring dihedral angle is 85.6 (9)°. The torsion angles O(10)—C(9)—C(8)—O(71) and O(10)—C(9)—C(8)—O(72) are markedly different [+143.5 (9), +17.8 (9)° respectively].

This orientation of the carboxylic acid group is in contrast to that found for (II) where the plane of the acid group lies approximately perpendicular to the plane of O(71)—C(8)—O(72) with the torsion angles O(10)—C(9)—C(8)—O(71) and O(10)—C(9)—C(8)—O(72) being -114.7 (9) and +130.8 (9)°. In the analogous acid 2,2-bis(4-chlorophenyl)acetic acid (DDA), (Shields & Kennard, 1977; Hovmöller, Norrestam & Palm, 1977), the same perpendicular orientation is found. The dihedral angles between the planes of the benzene rings and those between the benzene rings and the carboxylic acid plane are 59.7 (9), 48.3 (9), 44.9 (9)° (this compound) and 75.5, 85.6, 49.6° (DDA), although in (II) the benzene rings are removed a further oxygen from the carboxylic acid group compared with DDA. A further contrast in (II) is the lack of C—C—O angle distortion within the carboxylic acid group where the two angles are 117.8 (8) and 117.4 (7)°, suggesting that the group is disordered to some degree. However, the retention of discrete C—O distances [1.202 (11), 1.289 (11) Å] typical of normal carboxylic acid groups, with no tendency towards equality, allows identification of the two oxygens as 'carbonyl' [O(10)] and 'hydroxyl' [O(11)] respectively. Although this similarity in C—C—O angles has no precedence among the phenoxy acids, the relationship between contraction in the difference between C—C—O angles and C—O distances for the aromatic carboxylic acids is known (Dieterich, Paul & Curtin, 1974). Leiserowitz (1976) lists as one of the reasons for disorder in carboxylic acid groups the presence of close intermolecular O...O distances outside the dimer unit. This appears to be the reason for the effect in this example where a relatively close interaction [2.663 (Å)] between O(10) and O(11)' (outside the dimer unit) exists.

Normal *exo* C(1) angle distortion occurs for (II) [113.0 (9), 123.4 (8)° and 115.9 (7), 123.4 (8)° for rings (1) and (2) respectively].

Torsion angles about bonds in the oxoacetic acid side chain are listed in Table 4 and show the gross conformational differences between (I) and (II) and are compared with (2-chlorophenoxy)acetic acid (OCPA) (Kennard & Smith, 1981) and (±)-2-(2-chlorophenoxy)propionic acid (OCPPA) (Smith, Kennard & White, 1981). OCPA is essentially planar, which is the preferred molecular conformation of the majority of the phenoxyacetic acid analogues. In contrast, all 2-propionic acid analogues, including OCPPA, have the conformation with the α -substituted methyl group lying approximately in the plane of the benzene ring and the carboxylic acid group approximately perpendicular. In

Table 4. Torsion angles ($^{\circ}$) about bonds in the oxyacetic acid residues for (I) and (II) compared with those for (2-chlorophenoxy)acetic acid (OCPA) (Kennard & Smith, 1981) and (\pm)-2-(2-chlorophenoxy)propionic acid (OCPPA) (Smith, Kennard & White, 1981)

	(I)	(II)	OCPA		OCPPA
			Molecule A	Molecule B	
O(10)—C(9)—C(8)—O(71)	+143.5 (9)	-114.7 (9)	-179.3	-179.9	+161.0
O(10)—C(9)—C(8)—O(72)	+17.8 (9)	+130.8 (9)			
C(9)—C(8)—O(71)—C(11)	+164.7 (9)	+109.9 (9)	-175.1	+173.2	-66.3
C(9)—C(8)—O(72)—C(12)	+74.3 (9)	-165.5 (9)			
C(8)—O(71)—C(11)—C(21)	+179.2 (9)	+144.5 (9)	-179.4	+179.9	+179.0
C(8)—O(72)—C(12)—C(22)	+160.2 (9)	-178.5 (9)			

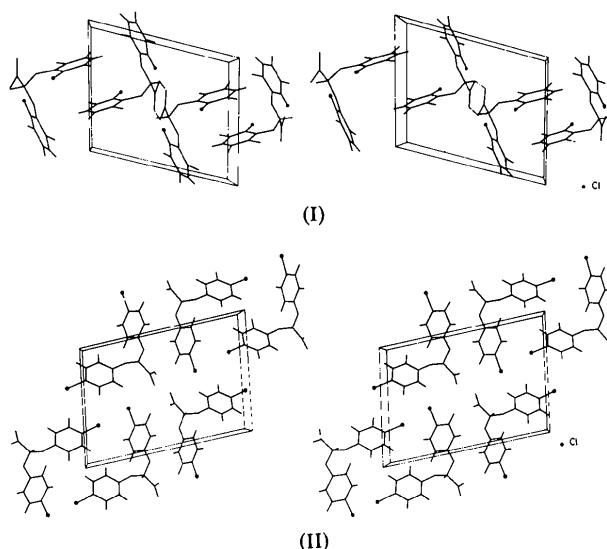


Fig. 3. Stereoviews perpendicular to the *ab* plane for (I) and (II). The origin is at the rear, lower, lefthand corner with *b* running vertically.

(I) and (II), a second phenoxy residue replaces the α -methyl of the 2-propionic acids and exerts a similar influence on the conformational aspects of these acids. In (I), however, the 2-chloro substituent groups of the ring orient symmetrically and are mutually *trans* with the ring to α -carbon separations [C(8) \cdots C(61), C(8) \cdots C(62)] being 2.826 and 2.929 (8) Å respectively. The result is that the two phenoxy groups have approximate twofold rotational symmetry about C(8).

Similar C(8) \cdots C(6) separations of 2.806 and 2.878 (12) Å are found for (II) although the change in conformation with the change in the ring-chlorine substitution from the 2 to the 4 positions is considerable. It is therefore likely that the perpendicular orientation of the carboxylic acid group [as in (II) or DDA] is energetically favoured and the ring orientation is consequential. In (I), the presence of the 2-chlorines in the rings forces the parallel orientation which results in the chlorines assuming the most favoured interactive positions with respect to the acid group.

Fig. 3 shows stereoviews of the unit-cell contents for (I) and (II).

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