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Structural Aspects of Phenoxyalkanoic Acids. The Structures of Phenoxyacetic Acid, (±)-2-Phenoxypropionic Acid, (±)-2-(4-Chlorophenoxy)propionic Acid, 2-Methyl-2-phenoxypropionic Acid and 2-(4-Chlorophenoxy)-2-methylpropionic Acid

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Abstract

The crystal structures of phenoxyacetic acid (I), (±)-2-phenoxypropionic acid (II), (±)-2-(4-chlorophenoxy)propionic acid (III), 2-methyl-2-phenoxypropionic acid (IV), and 2-(4-chlorophenoxy)-2-methylpropionic acid (V) have been determined from X-ray diffractometer data. Crystals of the five compounds are monoclinic with, for (I), $a = 12{\cdot}39$ (1), $b = 5{\cdot}114$ (6), $c = 11{\cdot}71$ (1) Å, $\beta = 91{\cdot}36$ (8)°, $V = 741{\cdot}8$ Å^3; $P2_1/c$, $Z = 4$; for (II), $a = 11{\cdot}07$ (1), $b = 5{\cdot}275$ (7), $c = 29{\cdot}22$ (3) Å, $\beta = 98{\cdot}17$ (8)°, $V = 1689{\cdot}0$ Å^3; $A2/a$, $Z = 8$; for (III), $a = 11{\cdot}533$ (2), $b = 5{\cdot}167$ (1), $c = 31{\cdot}91$ (1) Å, $\beta = 99{\cdot}35$ (2)°, $V = 1876{\cdot}3$ Å^3; $A2/a$, $Z = 8$; for (IV), $a = 14{\cdot}099$ (6), $b = 5{\cdot}698$ (3), $c = 11{\cdot}700$ (5) Å, $\beta = 91{\cdot}19$ (4)°, $V = 939{\cdot}7$ Å^3; $P2_1/n$, $Z = 4$; for (V), $a = 21{\cdot}127$ (8), $b = 7{\cdot}966$ (5), $c = 6{\cdot}329$ (3) Å, $\beta = 90{\cdot}05$ (4)°, $V = 1065{\cdot}2$ Å^3; $P2_1/n$, $Z = 4$. The structures were determined by direct methods and refined by full-matrix least squares to $R = 0{\cdot}046$, 0·059, 0·051, 0·055 and 0·060 for 869, 934, 1165, 1287 and 955 observed reflections for (I), (II), (III), (IV) and (V) respectively. All acids form hydrogen-bonded cyclic dimers with O—H···O distances of 2·629 (4) (I), 2·664 (6) (II), 2·657 (7) (III), 2·665 (4) (IV) and 2·627 (4) (V) Å. Phenoxyacetic acid is essentially a planar molecule while in the propionic acids (II) and (III), which are structurally similar but not isomorphous to one another, the β-methyl group lies approximately in the plane of the phenoxy group with the plane of the carboxylic acid residue synclinally related in a manner similar to all known 2-phenoxypropionic acids. Acids (IV) and (V) are conformationally similar to (II) and (III) in this respect but possess a different overall conformational motif for the oxo-alkanoic acid side chain due to the steric effects of the additional methyl group on the α carbon. Phenoxyacetic acid exhibits disorder in the carboxylic acid group with the two C—O distances equal and the proton disordered in the O···H···O hydrogen bond (O—H, 1·36 Å). No such disorder was found for the other acids.

Introduction

The phenoxyalkanoic acids comprise an important series of organic compounds of which several halogenated analogues are commercially available as auxin or 'hormone' herbicides. The most important of these are 2,4-D [(2,4-dichlorophenoxy)acetic acid], 2,4,5-T [(2,4,5-trichlorophenoxy)acetic acid], MCPA [(4-chloro-2-methylphenoxy)acetic acid] and the 2-phenoxy-substituted propionic analogues (2,4-DP, 2,4,5-TP and MCPP). The corresponding 2-methyl-2-phenoxypropionic acids, the α-phenoxyisobutyric acids, are inactive as herbicides and are in fact auxin antagonists (Jonsson, 1953). They do, however, possess anti-lipolytic and anti-hypocholestolaemic activity, and are used therapeutically under the names Clofibric acid [2-(4-chlorophenoxy)-2-methylpropionic acid] and Clofibrin (the ethyl ester) (Thorp, 1962). The basic aluminium salt of 2-methyl-2-phenoxypropionic acid, medically known as Atherolip, has been used to treat atherosclerosis (*Merck Index*, 1968). The parent compound, α-phenoxyisobutyric acid, is also reported to have comparable blood-cholesterol-lowering properties (Witiak, Chun-Lun Ho, Hackney & Connor, 1968).

It has been calculated (Zeelen, 1976) that the preferred conformation for both α-phenoxyisobutyric

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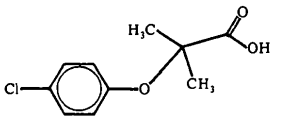
acid and its *p*-chloro analogue is the one with the benzene ring lying perpendicular to the plane containing the ether oxygen, the α carbon and one methyl carbon, with the carboxyl carbon and the second methyl carbon anticlinal (120°) to the benzene group. The two carboxyl oxygens lie in the plane defined by the ether oxygen, the α carbon and the carboxyl carbon.



This series examines the changes in the stereochemical aspects of the molecules with a change in the number and position of the halogen ring substituents and variation of the alkanoic acid residue.

Crystal data*

(I) $C_8H_8O_3$, $M_r = 152{\cdot}1$, $F(000) = 320$, $D_x = 1{\cdot}362$, $D_o = 1{\cdot}36$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·11 mm^{-1}, absent reflections $h0l$, l odd, and $0k0$, k odd; space group $P2_1/c$ (C_{2h}^5, No. 14), $2\theta_{max} = 50°$, 1585 independent reflections.

(II) $C_9H_{10}O_3$, $M_r = 166{\cdot}2$, $F(000) = 704$, $D_x = 1{\cdot}307$, $D_o = 1{\cdot}29$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·11 mm^{-1}, absent reflections $h0l$, h odd, and hkl,$k + l$ odd; space group $A2/a$ [variant of $C2/c$ (C_{2h}^6, No. 15)], $2\theta_{max} = 50°$, 1544 independent reflections.

(III) $C_9H_9ClO_3$, $M_r = 200{\cdot}6$, $F(000) = 832$, $D_x = 1{\cdot}426$, $D_o = 1{\cdot}41$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·38 mm^{-1}, absent reflections $h0l$, h odd, and hkl, $k + l$ odd; space group $A2/a$, $2\theta_{max} = 50°$, 1510 independent reflections.

(IV) $C_{10}H_{12}O_3$, $M_r = 180{\cdot}2$, $F(000) = 384$, $D_x = 1{\cdot}273$, $D_o = 1{\cdot}26$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·10 mm^{-1}, absent reflections $h0l$, $h + l$ odd, and $0k0$, k odd; space group $P2_1/n$ [variant of $P2_1/c$ (C_{2h}^5, No. 14)], 1565 independent reflections.

(V) $C_{10}H_{11}ClO_3$, $M_r = 214{\cdot}7$, $F(000) = 448$, $D_x = 1{\cdot}338$, $D_o = 1{\cdot}32$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·34 mm^{-1}, absent reflections $h0l$, $h + l$ odd, and $0k0$, k odd; space group $P2_1/n$, 1272 independent reflections.

Experimental

Compounds (I), (II) and (III) were prepared using the general method of Synerholm & Zimmerman (1945) by reacting the appropriate sodium phenoxide with ethyl bromoacetate [(I)] or ethyl 2-bromopropionate [(II) and (III)] in absolute ethanol followed by base hydrolysis. Compounds (IV) and (V) were obtained by

* See also *Abstract.*

Table 1. *Atomic coordinates* ($\times 10^4$) *with estimated standard deviations in parentheses*

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

	x	y	z	B_{eq} (Å^2)
(I) Phenoxyacetic acid				
C(1)	7619 (2)	−3104 (5)	3644 (2)	3·3 (2)
C(2)	8326 (2)	−4586 (6)	4322 (2)	3·9 (2)
C(3)	8967 (2)	−6447 (6)	3818 (3)	4·5 (2)
C(4)	8927 (2)	−6836 (6)	2647 (3)	4·5 (2)
C(5)	8221 (2)	−5367 (6)	1985 (3)	4·3 (2)
C(6)	7563 (2)	−3484 (6)	2469 (2)	3·7 (2)
O(7)	7001 (2)	−1326 (4)	4223 (1)	3·8 (2)
C(8)	6329 (2)	309 (6)	3530 (2)	3·3 (2)
C(9)	5769 (2)	2308 (5)	4241 (2)	3·2 (2)
O(10)	5908 (2)	2375 (4)	5315 (2)	4·2 (2)
O(11)	5165 (2)	3859 (4)	3687 (1)	4·0 (2)
H(6)	7015	−2317	1924	
H(5)	8204	−5717	1080	
H(4)	9352	−8532	2211	
H(3)	9510	−7600	4359	
H(2)	8352	−4232	5227	
H(81)	6833	1334	2936	
H(82)	5681	−989	3123	
(II) (±)-2-Phenoxypropionic acid				
C(1)	2089 (5)	3948 (10)	1467 (2)	2·8 (3)
C(2)	2834 (5)	2254 (11)	1751 (2)	3·3 (3)
C(3)	2315 (5)	736 (11)	2058 (2)	3·7 (3)
C(4)	1084 (6)	867 (11)	2087 (2)	3·9 (3)
C(5)	360 (5)	2557 (12)	1806 (2)	3·9 (3)
C(6)	861 (5)	4089 (11)	1492 (2)	3·3 (3)
O(7)	2699 (3)	5303 (7)	1170 (1)	3·2 (3)
C(8)	2052 (5)	7259 (10)	899 (2)	2·4 (3)
C(9)	1137 (5)	6189 (11)	516 (2)	3·1 (3)
O(10)	1234 (4)	4063 (7)	354 (1)	4·3 (3)
O(11)	272 (3)	7753 (8)	363 (1)	4·2 (3)
C(121)	3004 (5)	8741 (11)	689 (2)	3·9 (3)
H(2)	3808	2322	1774	
H(3)	2920	−330	2309	
H(4)	604	−297	2311	
H(5)	−588	2647	1812	
H(6)	225	5233	1273	
H(81)	1548	8482	1112	
H(11)	−416	7233	75	
H(121)	3635	9076	932	
H(122)	3458	7607	502	
H(123)	2754	9772	492	
(III) (±)-2-(4-Chlorophenoxy)propionic acid				
C(1)	−860 (6)	4081 (15)	1351 (2)	2·9 (4)
C(2)	−1325 (6)	2441 (15)	1626 (2)	3·4 (4)
C(3)	−595 (6)	948 (16)	1918 (2)	3·4 (4)
C(4)	612 (6)	1110 (15)	1928 (2)	3·2 (4)
C(5)	1097 (6)	2738 (15)	1659 (2)	3·8 (4)
C(6)	360 (6)	4224 (16)	1364 (2)	3·8 (4)
O(7)	−1678 (4)	5411 (10)	1075 (1)	3·4 (4)
C(8)	−1290 (6)	7424 (15)	821 (2)	3·3 (4)
C(9)	−706 (6)	6262 (14)	465 (2)	3·2 (4)
O(10)	−927 (5)	4111 (11)	319 (2)	4·7 (4)
O(11)	14 (4)	7848 (11)	325 (2)	4·4 (4)
C(121)	−2410 (7)	8860 (17)	621 (2)	4·2 (4)
Cl(4)	1539 (2)	−794 (5)	2291 (1)	4·4 (4)
H(2)	−2177	2294	1586	
H(3)	−797	−477	2119	
H(5)	1945	2805	1685	
H(6)	755	5650	1168	
H(81)	−599	8721	1022	

Table 1 (*cont.*)

	x	y	z	B_{eq} (Å^2)
H(11)	−327	2624	−73	
H(121)	−2741	9488	868	
H(122)	−2932	7476	429	
H(123)	−2167	10124	442	
(IV) 2-Methyl-2-phenoxypropionic acid				
C(1)	982 (2)	7323 (7)	3538 (3)	2·4 (2)
C(2)	1463 (3)	5703 (7)	4220 (3)	2·9 (2)
C(3)	2397 (3)	6138 (8)	4555 (3)	3·7 (2)
C(4)	2847 (3)	8192 (9)	4229 (4)	3·8 (2)
C(5)	2355 (3)	9826 (8)	3567 (3)	3·3 (2)
C(6)	1415 (3)	9406 (7)	3215 (3)	2·8 (2)
O(7)	78 (2)	6634 (5)	3225 (2)	2·9 (2)
C(8)	−592 (2)	8239 (7)	2714 (3)	2·7 (2)
C(9)	−272 (2)	9057 (7)	1530 (3)	2·6 (2)
O(10)	−560 (2)	10937 (5)	1146 (2)	3·7 (2)
O(11)	237 (2)	7588 (5)	972 (2)	3·7 (2)
C(121)	−817 (3)	10270 (8)	3497 (3)	3·6 (2)
C(122)	−1469 (3)	6706 (9)	2487 (4)	3·9 (2)
H(2)	1118	4013	4406	
H(3)	2783	4806	5021	
H(4)	3565	8345	4383	
H(5)	2678	11564	3278	
H(6)	1037	10803	2702	
H(11)	409	8191	−45	
H(121)	−1259	11202	3130	
H(122)	−303	11384	3590	
H(123)	−998	9536	4198	
H(124)	−1974	7728	2193	
H(125)	−1796	6343	3196	
H(126)	−1333	5370	2015	
(V) 2-(4-Chlorophenoxy)-2-methylpropionic acid				
Cl(4)	1378 (1)	2528 (3)	7400 (3)	3·8 (4)
C(1)	3051 (2)	2407 (8)	11767 (9)	4·3 (4)
C(2)	2491 (2)	3126 (8)	12477 (9)	4·9 (4)
C(3)	1962 (3)	3146 (8)	11077 (9)	4·5 (4)
C(4)	2037 (3)	2502 (8)	9066 (9)	5·1 (4)
C(5)	2601 (3)	1841 (9)	8376 (9)	5·1 (4)
C(6)	3109 (3)	1789 (9)	9750 (10)	4·4 (4)
O(7)	3515 (2)	2263 (5)	13304 (6)	4·1 (3)
C(8)	4150 (3)	2851 (8)	12882 (9)	3·6 (4)
C(9)	4510 (3)	1578 (8)	11552 (9)	5·1 (4)
O(10)	4905 (2)	2076 (5)	10269 (7)	4·9 (4)
O(11)	4396 (2)	23 (5)	11921 (7)	5·7 (4)
C(121)	4160 (3)	4594 (8)	11903 (12)	6·5 (5)
C(122)	4458 (3)	2829 (10)	15091 (11)	6·8 (5)
H(2)	2399	3524	13955	
H(3)	1522	3613	11505	
H(5)	2550	1010	6939	
H(6)	3481	1311	8818	
H(11)	4709	955	10760	
H(121)	3907	4603	10817	
H(122)	3830	5191	12686	
H(123)	4585	4799	12022	
H(124)	4414	1891	15496	
H(125)	4389	3756	15206	
H(126)	4849	3130	14817	

the modified Galimberti & Defranceschi (1947) procedure, reacting the appropriate phenol, sodium hydroxide, acetone and chloroform (Gilman & Wilder, 1955). Crystals suitable for X-ray analysis were grown from a toluene–chloroform mixture [(I), (II) and (III)] or hexane [(IV) and (V)] as colourless plates or prisms. The data crystals measured 0·40 × 0·50 × 0·12 mm (I); 0·40 × 0·40 × 0·16 mm (II); 0·40 × 0·40 × 0·20 mm (III); 0·30 × 0·45 × 0·50 mm (IV) and 0·25 × 0·40 × 0·31 mm (V).

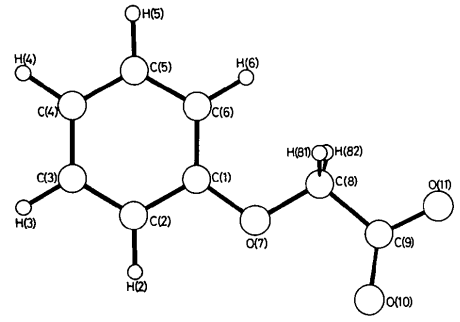
Three-dimensional X-ray diffraction data were obtained with monochromatized Mo $K\alpha$ radiation using a Syntex $P\bar{1}$ four-circle diffractometer. Unique data sets were collected in the range $2\theta < 50°$ by conventional 2θ–θ scans of which 869 (I), 934 (II), 1165 (III), 1287 (IV) and 955 (V) with $I > 2{\cdot}5\sigma(I)$ were considered observed and used in structure solution and refinement. No corrections were made for absorption. For (III), (IV) and (V) some intense reflections appeared to be seriously affected by extinction and were removed before the final cycle of refinement.

The structures were solved by direct methods using the centrosymmetric direct-methods approach incorporated in *SHELX* (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms reduced R [$= \sum |F_o - |F_c|| / \sum F_o$] to 0·046 (I), 0·059 (II), 0·051 (III), 0·055 (IV) and 0·060 (V). Unit weights were used. All H positions, except the carboxylic acid proton [H(11)] for (I) were located in difference-Fourier syntheses and were included in the calculations at fixed positions with the values of their isotropic U fixed at 0·05 Å^2. A peak, located in the difference map for (I) at distances of 1·36 and 1·27 Å from O(11) and O(10′) (the carbonyl oxygen of the symmetry-related carboxylic acid group) respectively with an O(11)—H(11)—O(10′) angle of 175·4°, was included in the refinement. It is considered in this example that the position of the proton is disordered and that the charge on the carboxyl group is delocalized. A final difference synthesis showed no electron density greater than 0·051 (I), 0·130 (II), 0·119 (III), 0·112 (IV) and 0·131 (V) e Å^{-3}. Atomic scattering factors for Cl, O and C were taken from Doyle & Turner (1968) and for H from Stewart, Davidson & Simpson (1965). Atomic parameters are listed in Table 1.*

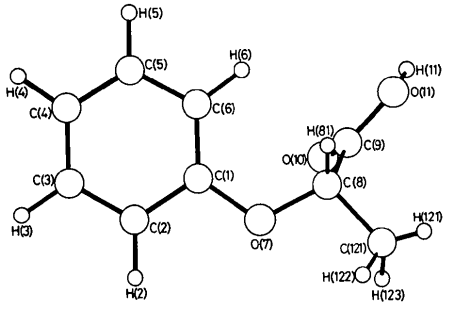
Discussion

Bond distances and angles for compounds (I) to (V) are given in Table 2 and the molecular conformation and numbering are illustrated in Fig. 1 (*a*) to (*d*). All acids form hydrogen-bonded cyclic dimers with O···O distances of 2·629 (4), 2·664 (6), 2·657 (7), 2·665 (4) and 2·627 (4) Å for (I) to (V) respectively. These

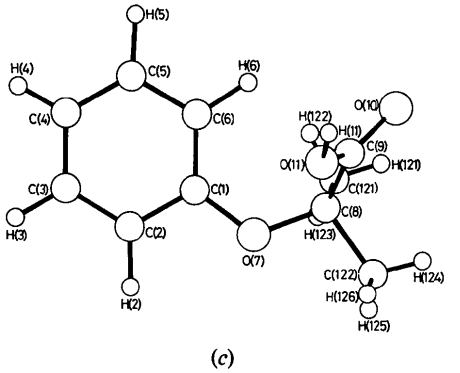
* Lists of structure factors and anisotropic thermal parameters for these compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36427 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



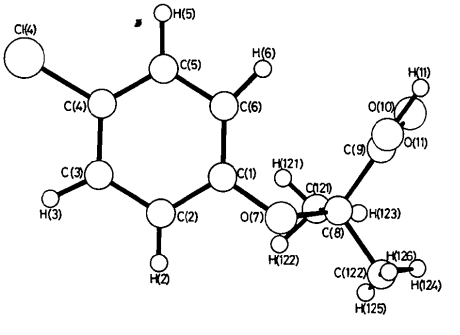
(*a*)



(*b*)



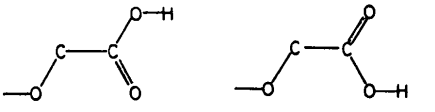
(*c*)



(*d*)

Fig. 1. Molecular configuration and numbering for (I), (II), (III), (IV) and (V) shown in views perpendicular to the plane of the benzene rings. For (I), H(11) is omitted. (*a*) Phenoxyacetic acid (I). (*b*) (±)-2-Phenoxypropionic acid (II) and (±)-2-(4-chlorophenoxy)propionic acid (III). (*c*) 2-Methyl-2-phenoxypropionic acid (IV). (*d*) 2-(4-Chlorophenoxy)-2-methylpropionic acid (V).

distances are comparable to those for phenoxyalkanoic acids (mean, 2·645 Å) (Table 3), and substituted benzoic acids (mean, 2·644 Å) (Smith & Kennard, 1979). Compounds (I), (II) and (III) adopt the synplanar–synplanar (*syn–syn*) conformation (*a*). This is found in the analogous α,β-saturated carboxylic acids (Leiserowitz, 1976), the 2-phenoxypropionic acids and in all the phenoxyacetic acids. However, acids (IV) and (V) adopt the synplanar–antiplanar (*syn–anti*) conformation (*b*), which is also found in two aryloxyisobutyric acids, 2-(4-dibenzofuryloxy)-2-methylpropionic acid (Wägner & Malmros, 1979*a*) and 2-methyl-2-[4-(phenoxy)phenoxy]propionic acid (Wägner & Malmros, 1979*b*)].



(*a*) *syn–syn* (*b*) *syn–anti*

The non-bonding distance O(ether)···O(carbonyl) is comparatively constant throughout the phenoxy series (Smith & Kennard, 1979) {range 2·605 Å [(2,4,5-trichlorophenoxy)acetic acid] to 2·775 Å [2-(4-chlorophenoxy)propionic acid]; mean 2·711 Å} and appears to be a preferred distance irrespective of the conformation of the side chain about the α carbon. For (IV) and (V), the O(ether)···O(carboxyl) distances are 2·705 and 2·723 Å respectively. There are no intermolecular contacts which are sufficiently close to be considered the cause of the conformational difference. However, non-bonding C—H···O contacts between C(121) and its hydrogens and O(10) or O(11) are relatively short and are similarly disposed with respect to the carboxyl group for (IV) and (V) (Table 3).

The preferred conformation for phenoxypropionic acids is to have one α-methyl group [C(122)] lying approximately in the plane of the phenoxy group [0·009 Å (IV) and 0·448 Å (V)] with the second methyl group adopting an energetically favoured position. In (IV) and (V), C(121) is located almost identically with respect to the carboxyl group, resulting in the internal adjustment of the side chain giving the conformational differences in the two acids (Table 3). These differences may also be due in part to the presence of the *p*-chlorine [Cl(4)] in (V) which interacts with C(121) having an intermolecular contact of 3·764 Å [Cl(4)···H(121), 3·15 Å]. No contacts between C(121) and C(4) less than 4 Å were found. The analogous isostructural phenoxypropionic acids (II) and (III) have conformations which maintain the relatively longer O(10)···C(121) and O(11)···C(121) distances [3·227, 3·137 Å (II); 3·215, 3·083 Å (III)] without showing any comparable changes in torsion angles. Phenoxyacetic acid (I) adopts the planar

Table 2. *Interatomic distances* (Å) *and angles* (°) *for phenoxyacetic acid* (I), (±)-2-*phenoxypropionic acid* (II), (±)-2-(4-*chlorophenoxy*)*propionic acid* (III), 2-*methyl*-2-*phenoxypropionic acid* (IV) *and* 2-(4-*chlorophenoxy*)-2-*methylpropionic acid* (V) *with estimated standard deviations in parentheses*

	(I)	(II)	(III)	(IV)	(V)
C(1)–C(2)	1·393 (4)	1·405 (7)	1·389 (8)	1·388 (5)	1·390 (6)
C(2)–C(3)	1·381 (4)	1·388 (8)	1·385 (9)	1·389 (5)	1·425 (6)
C(3)–C(4)	1·385 (4)	1·379 (8)	1·390 (8)	1·389 (6)	1·382 (6)
C(4)–C(5)	1·377 (4)	1·388 (8)	1·383 (9)	1·388 (6)	1·375 (8)
C(4)–Cl(4)	–	–	1·746 (6)	–	1·746 (6)
C(5)–C(6)	1·391 (4)	1·395 (8)	1·392 (9)	1·400 (5)	1·381 (8)
C(6)–C(1)	1·389 (4)	1·374 (7)	1·403 (8)	1·391 (5)	1·374 (8)
C(1)–O(7)	1·378 (3)	1·374 (6)	1·367 (7)	1·376 (7)	1·385 (6)
O(7)–C(8)	1·421 (3)	1·430 (6)	1·434 (7)	1·436 (4)	1·445 (6)
C(8)–C(9)	1·499 (4)	1·508 (7)	1·534 (8)	1·538 (5)	1·523 (8)
C(8)–C(121)	–	1·512 (7)	1·536 (9)	1·514 (6)	1·521 (9)
C(8)–C(122)	–	–	–	1·532 (5)	1·542 (8)
C(9)–O(10)	1·266 (3)	1·229 (6)	1·216 (8)	1·227 (4)	1·231 (6)
C(9)–O(11)	1·260 (3)	1·294 (6)	1·297 (7)	1·289 (4)	1·283 (7)
O(10)···O(11′)	2·629 (3)	2·664 (6)	2·657 (7)	2·665 (4)	2·627 (6)
C(1)–C(2)–C(3)	119·4 (3)	119·1 (5)	120·7 (6)	119·6 (4)	118·1 (5)
C(2)–C(3)–C(4)	121·0 (3)	120·9 (8)	118·6 (6)	120·6 (4)	118·5 (5)
C(3)–C(4)–C(5)	119·1 (3)	119·3 (8)	121·8 (6)	119·5 (4)	122·4 (5)
C(4)–C(5)–C(6)	121·2 (3)	120·7 (5)	119·4 (6)	120·6 (4)	119·0 (5)
C(5)–C(6)–C(1)	118·9 (3)	119·5 (5)	119·4 (6)	119·0 (4)	120·4 (5)
C(6)–C(1)–C(2)	120·4 (3)	120·5 (5)	120·1 (6)	120·8 (3)	121·6 (5)
C(6)–C(1)–O(7)	124·4 (2)	125·8 (5)	125·2 (5)	125·3 (3)	124·0 (5)
C(2)–C(1)–O(7)	115·3 (2)	113·8 (5)	114·6 (5)	113·7 (3)	114·2 (4)
C(1)–O(7)–C(8)	115·6 (2)	118·2 (4)	118·9 (4)	121·8 (3)	120·0 (4)
O(7)–C(8)–C(9)	110·9 (2)	111·9 (4)	110·5 (5)	111·5 (3)	110·6 (5)
O(7)–C(8)–C(121)	–	106·0 (4)	105·5 (5)	112·3 (3)	112·6 (3)
O(7)–C(8)–C(122)	–	–	–	103·3 (3)	102·7 (3)
C(8)–C(9)–O(10)	121·1 (2)	122·8 (5)	123·5 (6)	119·6 (3)	119·3 (5)
C(8)–C(9)–O(11)	114·8 (2)	113·8 (5)	113·0 (6)	115·9 (3)	116·6 (5)
C(9)–C(8)–C(121)	–	109·0 (4)	108·8 (5)	112·5 (3)	112·1 (5)
C(9)–C(8)–C(122)	–	–	–	105·5 (3)	106·4 (5)
O(10)–C(9)–O(11)	124·1 (3)	123·4 (5)	123·5 (6)	124·4 (3)	124·0 (5)
C(3)–C(4)–Cl(4)	–	–	119·0 (5)	–	117·4 (4)
C(5)–C(4)–Cl(4)	–	–	119·2 (5)	–	120·3 (5)
C(121)–C(8)–C(122)	–	–	–	111·2 (3)	112·0 (3)

conformation found for the majority of the phenoxyacetic acid analogues.

Comparative torsion angles [C(2)–C(1)–O(7)–C(8), C(1)–O(7)–C(8)–C(9) and O(7)–C(8)–C(9)–O(11)] for the phenoxyalkanoic acid series are listed in Table 3, together with important interatomic distances and angles.

Some structural trends are present. These are: (i) distortion of the *exo*-C(1) bond angles and (ii) abnormal values associated with the distances and angles about C(9) of the carboxyl group. Regarding point (i), the *exo* angles, C(2)–C(1)–O(7) and C(6)–C(1)–O(7) [115·3, 124·4° (I); 113·8, 125·8° (II); 114·6, 125·2° (III); 113·7, 125·3° (IV); 114·2, 124·0° (V)], significantly deviate from the expected trigonal angle. This is explained by a molecular crowding effect due to the steric requirements of the bulky oxoacetic or oxopropionic acid side chain. This has been observed previously for members of the substituted benzoic acid series. Furthermore the phenomenon is general among all other members of the series (Table 3). The deviation from the ideal stereochemistry is least for (IX) [(2,4,6-trichlorophenoxy)acetic acid] which has chlorine substituents in both *ortho* positions of the ring. This forces the side chain into an orientation with the carboxyl group intermediate between a planar conformation [torsion angle C(1)–O(7)–C(8)–C(9) *ca* ± 180°] and a synclinal conformation [torsion angle C(1)–O(7)–C(8)–C(9) *ca* ± 90°].

Regarding point (ii), it is considered that within the non-orientationally-disordered carboxylic acid group, the 'normal' C=O and C–OH bond distances are 1·21 and 1·31 Å respectively (Leiserowitz, 1976). Furthermore, the C–C=O angle approaches more closely the trigonal value (120°) than does the C–C–OH angle. The presence of disorder in the carboxylic acid group manifests itself in a contraction of the difference between the C=O and C–OH distances and the C–C=O and C–C–OH bond angles. This phenomenon is well documented among the benzoic acids (Leiserowitz, 1976) and a linear relationship

Table 3. *Comparative interatomic distances (Å) and angles (°) about the carboxylic acid side chain for the series of aryloxyalkanoic acids for which structural information is available*

The conformational system [synplanar (*syn*) or antiplanar (*anti*)] is defined by Leiserowitz (1976).

Distances

	C(9)–O(10)	C(9)–O(11)	C(8)–C(9)–O(10)	C(8)–C(9)–O(11)	O(7)–O(10) or O(7)–O(11)*	Conformational motif
(I)	1·266 (3)	1·260 (3)	121·1 (2)	114·8 (2)	2·671	*syn–syn*
(II)	1·229 (6)	1·294 (6)	122·8 (5)	113·8 (5)	2·766	*syn–syn*
(III)	1·216 (8)	1·297 (7)	123·5 (6)	113·0 (6)	2·775	*syn–syn*
(IV)	1·227 (4)	1·289 (4)	119·6 (3)	115·9 (3)	2·723*	*syn–anti*
(V)	1·231 (6)	1·283 (7)	119·3 (5)	116·6 (5)	2·705*	*syn–anti*
(VI)	1·217 (6)	1·304 (5)	124·5 (3)	112·2 (2)	2·717	*syn–syn*
(VII)	1·208 (5)	1·325 (4)	123·8 (3)	112·0 (2)	2·710	*syn–syn*
(VIII)	1·213 (7)	1·301 (8)	124·4 (4)	112·7 (3)	2·605	*syn–syn*
(IX)	1·234 (5)	1·262 (5)	123·3 (4)	115·7 (4)	2·683	*syn–syn*
(X)	1·237 (7)	1·276 (7)	124·0 (6)	115·3 (5)	2·745	*syn–syn*
(XI)	1·213 (3)	1·311 (4)	124·1 (3)	111·9 (3)	2·730	*syn–syn*
(XII)	1·238 (4)	1·277 (4)	122·3 (3)	114·4 (3)	2·700	*syn–syn*
(XIII)	1·214 (2)	1·306 (2)	123·2 (2)	112·3 (2)	2·739	*syn–syn*
(XIV)	1·224 (4)	1·309 (4)	121·3 (2)	115·3 (2)	2·717*	*syn–anti*
(XV)	1·239 (3)	1·286 (3)	120·0 (2)	116·3 (2)	2·708*	*syn–anti*
(XVI) (*a*)	1·25 (2)	1·32 (2)	125 (1)	113 (1)	2·514	*syn–syn*
(*b*)	1·25 (2)	1·35 (2)	129 (1)	110 (1)	2·501	*syn–syn*
(XVII) (*a*)	1·27 (4)	1·31 (4)	119 (1)	113 (1)	2·756	*syn–syn*
(*b*)	1·20 (4)	1·34 (4)	120 (1)	116 (1)	2·756	*syn–syn*

Torsion angles

	C(2)–C(1)–O(7)–C(8)	C(1)–O(7)–C(8)–C(9)	O(7)–C(8)–C(9)–O(11)	
(I)	+176·1	−175·1	+179·2	This work†
(II)	−173·8	−72·9	−158·2	
(III)	+171·1	+73·8	−156·8	
(IV)	+167·7	+65·6	+29·3	
(V)	−130·4	−79·0	+35·9	
(VI)	+179·1‡	+80·4‡	−173·1‡	Smith, Kennard & White (1976*a*)
(VII)	+188·5	+72·4	−178·3	Smith, Whitnall & Kennard (1976)
(VIII)	+174·2	−171·6	−179·6	Smith, Kennard & White (1976*b*)
(IX)	+108·7	−152·3	−151·1	Smith, Kennard & White (1977)
(X)	+181·8	+73·1	−148·9	Smith, Kennard & White (1978)
(XI)	+179·2	+71·3	−166·2	Smith, Kennard, White & Hodgson (1977)
(XII)	+161·3	+85·5	−180·6	Smith, Kennard, White & Hodgson (1980)
(XIII)	+181·0	+66·3	−161·0	Smith, Kennard & White (1981)
(XIV)	+25·5	−64·9	−35·9	Wägner & Malmros (1979*a*)
(XV)	+179·1	−58·0	−35·2	Wägner & Malmros (1979*b*)
(XVI) (*a*)	+178·9	−173·2	−177·5	Chandrasekhar & Pattabhi (1977)
(*b*)	−179·3	+172·3	+179·8	
(XVII) (*a*)	+171·8	+76·0	−158·8	Karle & Karle (1966)
(*b*)	−172·0	−76·4	+160·4	

(I) Phenoxyacetic acid; herbicidally inactive. (II) (±)-2-Phenoxypropionic acid; inactive. (III) (±)-2-(4-Chlorophenoxy)propionic acid; active. (IV) 2-Methyl-2-phenoxypropionic acid; inactive. (V) 2-(4-Chlorophenoxy)-2-methylpropionic acid; inactive. (VI) (2,4-Dichlorophenoxy)acetic acid; highly active. (VII) (2,5-Dichlorophenoxy)acetic acid; highly active. (VIII) (2,4,5-Trichlorophenoxy)acetic acid; highly active. (IX) (2,4,6-Trichlorophenoxy)acetic acid; inactive. (X) (±)-2-(3,5-Dichlorophenoxy)propionic acid; inactive. (XI) (±)-2-(2,4,5-Trichlorophenoxy)propionic acid; active. (XII) (±)-2-(4-Chloro-2-methylphenoxy)propionic acid; active. (XIII) (±)-2-(2-Chlorophenoxy)propionic acid; active. (XIV) 2-(4-Dibenzofuryloxy)-2-methylpropionic acid; inactive. (XV) 2-Methyl-2-[4-(phenoxy)-phenoxy]propionic acid; inactive. (XVI) (*a*), (*b*) 2-Chlorophenoxyacetic acid, molecules (*a*) and (*b*); active. (XVII) (*a*) (−)-2-(3-Bromophenoxy)propionic acid; inactive. (*b*) (+)-2-(3-Methoxyphenoxy)propionic acid; inactive.

† E.s.d.'s for these compounds range between 0·2–0·5°.
‡ E.s.d.'s not available for compounds (VI)–(XVII).

between difference in bond distances (Δr) and bond angles ($\Delta\theta$) has been found to exist for the same series (Dieterich, Paul & Curtin, 1974). There was only one example [phenoxyacetic acid (I)] in the phenoxyalkanoic acid series that exhibits disorder phenomenon in the carboxylic acid group. Although the acid proton

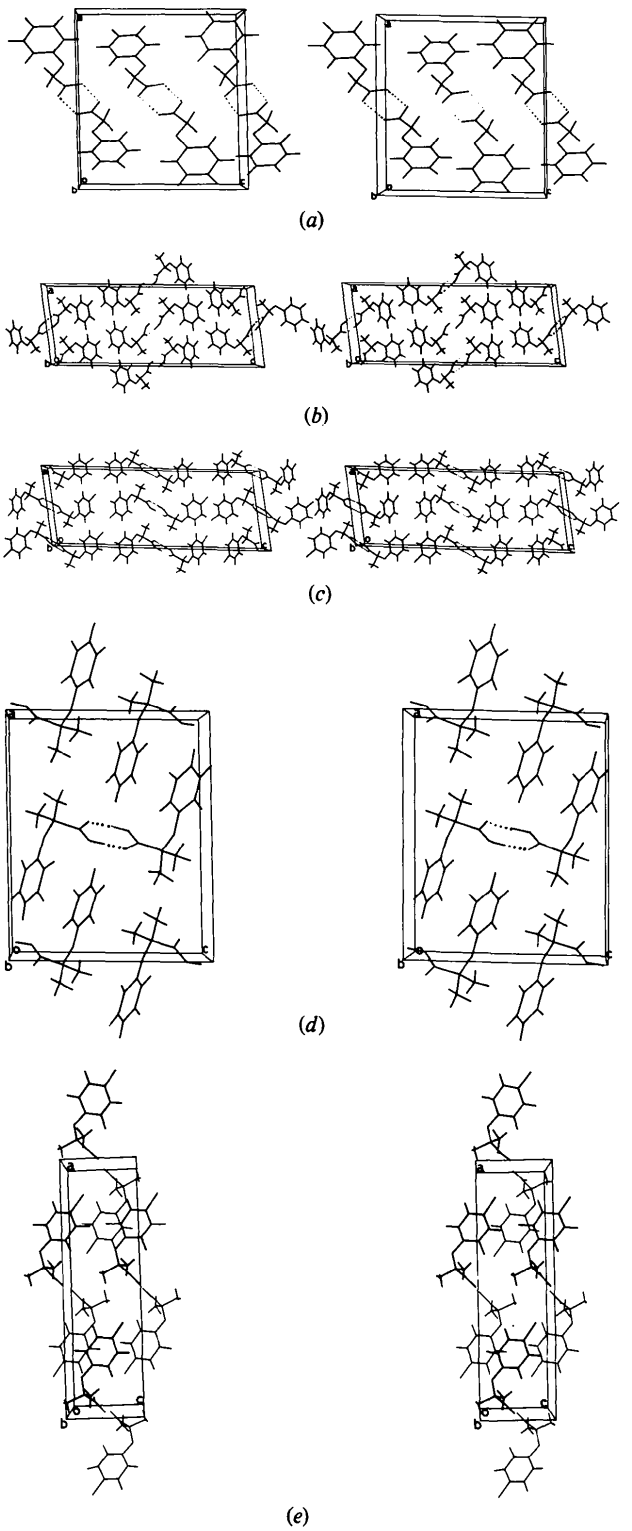


Fig. 2. Stereoscopic view of the packing of the molecules of (I), (II), (III), (IV) and (V) in the unit cells viewed down the *b* axes. (*a*) Phenoxyacetic acid (I). (*b*) (±)-2-Phenoxypropionic acid (II). (*c*) (±)-2-(4-Chlorophenoxy)propionic acid (III). (*d*) 2-Methyl-2-phenoxypropionic acid (IV). (*e*) 2-(4-Chlorophenoxy)-2-methylpropionic acid (V).

was located with a reasonable degree of certainty, its position, intermediate between the two oxygens in the O···O hydrogen bond [O(11)–H(11), 1·36 Å; O(10′)–H(11), 1·27 Å], was not refined. However, the C–O distances [1·260, 1·263 (3) Å] are indicative of a delocalized carboxyl system, although the C–C–O angles [C(8)–C(9)–O(10), 121·1 (2)°, and C(8)–C(9)–O(11), 114·8 (2)°] retain their identities as being derived from C–C=O and C–C–O(H) respectively. This assignment is further reinforced by the fact that the synclinal–synclinal conformational motif is found with no exceptions among the known phenoxyacetic acids. The reason for the disorder is not understood since no close intra- or intermolecular contacts involving carboxyl oxygens were found for (I).

The packing of acids (I) to (V) is shown in Fig. 2(*a*) to (*e*). The isostructural acids (II) and (III) have similar cells, with the *a* and *c* parameters larger to accommodate the *p*-chloro ring substituent (11·07 to 11·533 Å and 29·22 to 31·91 Å). These two acids are conformationally similar which probably accounts for the ease of formation of the quasi-racemates [(+) or (–)]-phenoxypropionic acid and [(–) or (+)]-2-(4-chlorophenoxy)propionic acid (Matell, 1954). However, the cells are subtly different and cannot be superimposed.

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References

CHANDRASEKHAR, K. & PATTABHI, V. (1977). *Acta Cryst.* B**33**, 1257–1260.

DIETERICH, D. A. PAUL, I. C. & CURTIN, D. Y. (1974). *J. Am. Chem. Soc.* **96**, 6372–6380.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

GALIMBERTI, P. & DEFRANCESCHI, A. (1947). *Gazz. Chim. Ital.* **77**, 431–438.

GILMAN, H. & WILDER, G. R. (1955). *J. Am. Chem. Soc.* **77**, 6644–6646.

JONSSON, A. (1953). *Acta Chem. Scand.* **7**, 596–602.

KARLE, I. L. & KARLE, J. (1966). *J. Am. Chem. Soc.* **88**, 24–27.

LEISEROWITZ, L. (1976). *Acta Cryst.* B**32**, 775–802.

MATELL, M. (1965). *Ark. Kemi*, **7**, 437–442.

Merck Index (1968). 8th ed., p. 1712. New Jersey: Merck & Co. Inc.

SHELDRICK, G. M. (1976). *SHELX* 76. A program for crystal structure determination. Univ. of Cambridge, England.

SMITH, G. & KENNARD, C. H. L. (1979). *J. Agric. Food Chem.* **27**, 779–786.
SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1976*a*). *J. Chem. Soc. Perkin Trans* 2, pp. 791–792.
SMITH, G. KENNARD, C. H. L. & WHITE, A. H. (1976*b*). *Aust. J. Chem.* **29**, 2727–2730.
SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1977). *Cryst. Struct. Commun.* **6**, 45–52.
SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1978). *Acta Cryst.* B**34**, 2885–2887.
SMITH, G., KENNARD, C. H. L. & WHITE, A. H. (1981). *Acta Cryst.* B**37**, 275–277.
SMITH, G., KENNARD, C. H. L., WHITE, A. H. & HODGSON, P. G. (1977). *Acta Cryst.* B**33**, 2922–2924.
SMITH, G. KENNARD, C. H. L., WHITE, A. H. & HODGSON, P. G. (1980). *Acta Cryst.* B**36**, 992–994.
SMITH, G. WHITNALL, J. & KENNARD, C. H. L. (1976). *Cryst. Struct. Commun.* **5**, 749–752.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
SYNERHOLM, M. E. & ZIMMERMAN, P. W. (1945). *Contrib. Boyce Thompson Inst.* **14**, 91–103.
THORP, J. M. (1962). *Lancet*, **1**, 1323–1326.
WÄGNER, A. & MALMROS, G. (1979*a*). *Acta Cryst.* B**35**, 2220–2222.
WÄGNER, A. & MALMROS, G. (1979*b*). *Acta Cryst.* B**35**, 2222–2225.
WITIAK, D. T., CHUN-LUN HO, T., HACKNEY, R. E. & CONNOR, W. E. (1968). *J. Med. Chem.* **11**, 1086–1089.
ZEELEN, F. J. (1976). *Quantitative Structure–Activity Relationships*, edited by M. TICHÝ, pp. 161–164. Basel: Springer.

Acta Cryst. (1982). B**38**, 875–880

Die Strukturen von 1,3-Dimethyl-3′,4′-diphenylimidazolidin-2-spiro-2′(2′*H*)-thiet-4,5-dion, 1,3-Dimethyl-4′,5′-diphenylimidazolidin-2-spiro-3′(3′*H*)-1′,2′-dithiol-4,5-dion und 1,3-Dimethyl-2-(1,2-diphenylethyl)imidazolidin-4,5-dion

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Abstract

The first two title compounds are obtained from the light-induced reaction of 1,3-dimethyl-2-thioparabanic acid in the presence of diphenylacetylene, whereas the third product resulted from treatment of the first with Raney nickel. The structure of 1,3-dimethyl-3′,4′-diphenylimidazolidine-2-spiro-2′(2′*H*)-thiete-4,5-dione ($C_{19}H_{16}N_2O_2S$) was solved by direct methods and refined by least-squares techniques to a residual R index of 0·047 based on 2131 observations with $I \geq 2\sigma(I)$. The compound crystallizes in the orthorhombic space group *Pbca*, with $a = 14{\cdot}164$ (3), $b = 12{\cdot}766$ (2), $c = 18{\cdot}736$ (3) Å, $Z = 8$, $U = 3387{\cdot}9$ Å^3, $D_m = 1{\cdot}32$ (1) and $D_x = 1{\cdot}32$ (1) Mg m^{-3}. Except for a long S–C(spiro) bond distance of 1·903 (3) Å other bond lengths are normal. Yellow crystals of 1,3-dimethyl-4′,5′-diphenylimidazolidine-2-spiro-3′(3′*H*)-1′,2′-dithiole-4,5-dione ($C_{19}H_{16}N_2O_2S_2$) belong to the monoclinic space group $P2_1/n$ with $a = 8{\cdot}352$ (1), $b = 9{\cdot}267$ (1), $c = 23{\cdot}285$ (1) Å, $\beta = 96{\cdot}942$ (6)°, $Z = 4$, $U = 1789{\cdot}1$ Å^3, $D_m = 1{\cdot}36$ (1) and $D_x = 1{\cdot}37$ (1) Mg m^{-3}. The structure was solved by the heavy-atom method. Anisotropic refinement (H atoms isotropic) converged with a final R value of 0·038 for the 3041 reflexions with $I \geq 2\sigma(I)$. The colorless crystals of 1,3-dimethyl-2-(1,2-diphenylethyl)imidazolidine-4,5-dione ($C_{19}H_{20}N_2O_2$) belong to the orthorhombic space group *Pbca* with $a = 12{\cdot}930$ (1), $b = 20{\cdot}643$ (2), $c = 12{\cdot}364$ (1) Å, $Z = 8$, $U = 3300{\cdot}1$ Å^3, $D_m = 1{\cdot}25$ (1) and $D_x = 1{\cdot}24$ (1) Mg m^{-3}. The structure was solved by direct methods and refined by least-squares methods yielding a conventional R value of 0·054 for 1909 reflexions with $I \geq 2\sigma(I)$

Einleitung

Das erste stabile, auf photochemischem Wege synthetisierte Thiet-Derivat (2) wird durch Bestrahlung der 1,3-Dimethyl-2-thioparabansäure (1) mit blauem Licht in Gegenwart von Diphenylacetylen als Ergebnis einer formalen (2 + 2)-Cycloaddition gebildet (Gotthardt & Huss, 1978; Gotthardt, Nieberl & Dönecke, 1980). Als Nebenprodukt entsteht noch die Spiro-Verbindung (3). Da die spektroskopischen Daten (IR, UV, ^{1}H-NMR, MS) von (2) sowie ein reduktives Abbauprodukt zunächst für ein Spiro[imidazolidin-2,2′-2-thianaphthalin]-Derivat sprachen (Gotthardt & Nieberl, 1976), überprüften wir Konstitution (2) durch eine

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