2-(4-Chlorophenoxy)propionic Acid

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Abstract. $C_9H_9ClO_3$, monoclinic, $C2/c$, $a = 31\cdot858$ (9), $b = 5\cdot171$ (1), $c = 11\cdot535$ (3) Å, $\beta = 99\cdot312$ (9)°, $V = 1876$ Å^3, $Z = 8$, $D_c = 1\cdot413$, $D_m = 1\cdot42$ Mg m^{-3}, $M_r = 200\cdot6$. The structure was solved by direct methods and refined to an R of $0\cdot074$ for 1002 counter reflections. The molecules exist as dimers linked by O—H$\cdots$O hydrogen bonds. The angle between the benzene ring and carboxyl-group planes is $81\cdot9$ (8)°.

Introduction. The crystal-structure analysis of 2-(4-chlorophenoxy)propionic acid (4-CPPA) was undertaken as part of research on the structure–activity relationships of plant-growth hormones. 4-CPPA is soluble in warm water and crystals were grown by slow evaporation. Weissenberg photographs showed the crystals to be monoclinic, space group $C2/c$ or Cc; the former was confirmed by intensity statistics, structure determination and refinement. Accurate cell parameters were obtained by a least-squares fit (Main & Woolfson, 1963) to the settings of 25 reflections measured at $\pm 2\theta$ on a Picker four-circle diffractometer. Intensities were measured in the θ–2θ mode ($2\theta \leq 130°$) with Fe-monochromated Co $K\alpha$ radiation ($\lambda = 1\cdot7903$ Å) at a scan rate of 2° min^{-1}. The scan range was 2° and backgrounds were measured for 10 s each on either side of the peak. The intensities were corrected for absorption (North, Phillips & Mathews, 1966).

The structure was solved by *MULTAN* (Main, Woolfson & Germain, 1971). An E map with the highest combined figure of merit (2·72) and lowest residual (19·47) revealed all the non-H atoms ($R = 0\cdot39$). Successive block-diagonal least-squares refinement (Shiono, 1968) of these atoms with isotropic temperature factors and unit weights for all reflections reduced R to 0·14. A difference Fourier map then revealed the eight H atoms close to their stereochemically expected positions and these were included in all subsequent structure-factor calculations with isotropic temperature factors of the atoms to which they are bonded. The H-atom parameters were not refined. Continued block-diagonal and full-matrix least-squares refinement

Table 1. *Fractional positional* ($\times 10^4$ *for non*-H, $\times 10^3$ *for* H) *and isotropic thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3} \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \beta_{ij}$ with $\sigma(B_{eq}) = \frac{4}{3} \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \sigma(\beta_{ij})$.

	x	y	z	B_{eq}/B (Å^2)
Cl	2710 (1)	10791 (4)	−1538 (2)	4·7 (1)
C(1)	3649 (2)	5925 (13)	859 (6)	3·4 (3)
C(2)	3372 (2)	7543 (14)	1309 (6)	4·0 (3)
C(3)	3086 (2)	9036 (14)	596 (6)	4·0 (3)
C(4)	3071 (2)	8902 (13)	−616 (6)	3·6 (3)
C(5)	3341 (2)	7284 (14)	−1087 (6)	4·4 (3)
C(6)	3634 (2)	5770 (14)	−356 (6)	4·2 (3)
O(7)	3921 (1)	4598 (9)	1668 (4)	4·0 (2)
C(8)	4179 (2)	2598 (13)	1285 (6)	4·0 (3)
C(9)	4383 (2)	1157 (15)	2405 (7)	5·0 (3)
C(10)	4536 (2)	3743 (15)	713 (6)	3·9 (3)
O(11)	4667 (1)	2155 (10)	−20 (5)	5·2 (2)
O(12)	4678 (1)	5879 (10)	931 (5)	5·3 (2)
H(C2)	347	763	226	4·2
H(C3)	279	1017	78	4·0
H(C5)	328	736	−209	4·6
H(C6)	385	455	−72	4·4
H(C8)	399	133	65	4·1
H1(C9)	456	258	300	5·1
H2(C9)	416	38	266	5·1
H3(C9)	458	−39	217	5·1
H(O11)	496	289	−26	5·1

(Gantzel, Sparks & Trueblood, 1961) of the non-H atoms with anisotropic thermal parameters led to a final R of 0·074.† Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). The final atomic parameters are listed in Table 1.

Discussion. The bond lengths and angles are shown in Fig. 1. The C—Cl distance of 1·736 (6) Å agrees well with the values observed in a series of phenoxy-alkanoic acids (Smith & Kennard, 1979; Smith, Kennard & White, 1981). Other interatomic distances and angles compare favourably with those reported for 2-(2,4,5-trichlorophenoxy)propionic acid (Smith, Ken-

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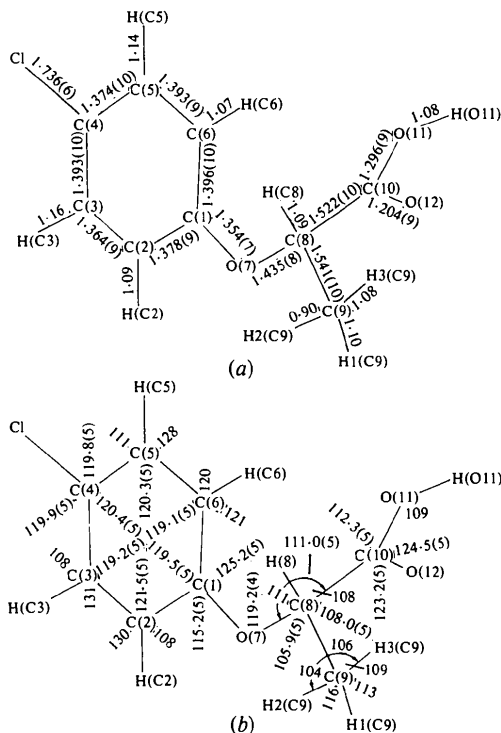
Fig. 1. (a) Bond lengths (Å) and (b) bond angles (°).

Fig. 2. Projection of the structure down b. Hydrogen bonds are shown by broken lines.

nard, White & Hodgson, 1977) and 2-(4-chloro-2-methylphenoxy)propionic acid (Smith, Kennard, White & Hodgson, 1980). The average bond length in the ring system is 1·383 (9) Å. The exo-C(1) angles C(2)—C(1)—O(7) [125·2 (5)°] and C(6)—C(1)—O(7) [115·2 (5)°] deviate appreciably from the trigonal value, as in several other members of this series of compounds (Smith & Kennard, 1979).

The angle between the least-squares planes through the benzene ring and carboxyl group is 81·9 (8)°, so that the molecule exists in the 'modulation' conformation defined by Kaethner (1977). Other plant hormones closely allied to 4-CPPA prefer the same conformation in the crystalline state, for example (2,4-dichlorophenoxy)acetic acid (85·2°; Smith, Kennard & White, 1976), (2,5-dichlorophenoxy)acetic acid (81·2°; Smith, Whitnall & Kennard, 1976), 2-(2,4,5-trichlorophenoxy)propionic acid (77·8°; Smith, Kennard, White & Hodgson, 1977), 2-(4-chloro-2-methyl-phenoxy)propionic acid (85·5°; Smith, Kennard, White & Hodgson, 1980) and 2-(2-chlorophenoxy)-propionic acid (76·7°; Smith, Kennard & White, 1981).

The torsion angle about the bond O(7)—C(8) is 73·6 (7)° giving rise to a synclinal conformation as in all propionic acid analogues studied to date (Smith & Kennard, 1979). This synclinal torsion angle invariably seems to dictate the 'modulation' (or perpendicular) conformation for plant hormones (Raghunathan & Pattabhi, 1981), while an antiperiplanar torsion angle
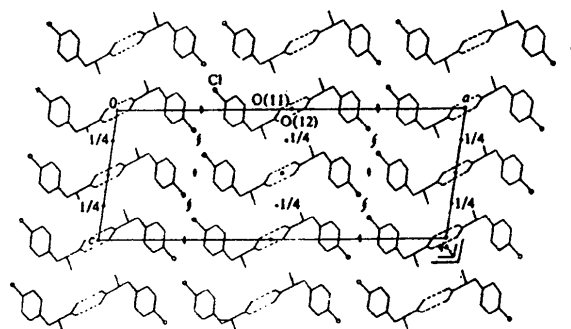
entails near-planarity of the molecule ('recognition' or parallel conformation).

The molecular packing is shown in Fig. 2. The molecules are linked in dimers across centres of symmetry by O–H⋯O hydrogen bonds. The O⋯O distance of 2·683 (9) Å and O–H⋯O angle of 166° compare well with values observed in other substituted phenoxy and benzoic acids (Smith & Kennard, 1979).

Note added in proof: It was brought to our notice, at the proof stage, that a paper on 2-(4-chlorophenoxy)-propionic acid has already appeared in this journal (Kennard, Smith & White, 1982). Cell parameters quoted by Kennard et al. are $a = 31·91$ (1), $b = 5·167$ (1), $c = 11·533$ (2) Å, $\beta = 99·35$ (2)°, and the data were collected using Mo $K\alpha$ radiation. The cell parameters b and c differ from our values of 4σ and 5σ respectively. The differences in the bond geometry of the molecule between the two studies are of the order of 1 to 2σ, which is insignificant.

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Structure of Agmatine Sulphate Dihydrate:* An Extensive Amine–Sulphate–Water Hydrogen-Bond Network

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Abstract. $C_5H_{14}N_4.H_2SO_4.2H_2O$, $M_r = 264.3$, orthorhombic, *Pbca*, $a = 22.251$ (16), $b = 7.199$ (5), $c = 15.849$ (11) Å, $Z = 8$, $D_m = 1.390$, $D_c = 1.383$ (3) Mg m^{-3}. The structure was solved by heavy-atom and Fourier methods and refined to $R = 0.060$ for 1311 counter reflections. The agmatine chain is essentially planar, packing in layers parallel to *ac*. An elaborate network of N–H$\cdots$O and O–H$\cdots$O hydrogen bonds interlinks the amine, water and sulphate groups.

Introduction. Some of the amines produced from amino acids by bacteria have pharmacological activity in animals (Fruton & Simmonds, 1965). These oligoamines are low molecular weight, aliphatic, non-protein, nitrogenous bases and include the simple diamines putrescine and cadaverine, the aminopropyl derivatives spermidine and spermine, and the peculiar guanidine bases such as agmatine and octopine found in invertebrate tissues and microbes. Oligoamines stimulate chain elongation in systems containing DNA-dependent RNA-polymerase *in vitro* and also have follicle-stimulating hormone-releasing-factor activity.

Agmatine sulphate dihydrate (ASD) (Fig. 1) was crystallized from aqueous methanol. Preliminary cell parameters were obtained from Weissenberg photographs and accurate values by least-squares refinement (Main & Woolfson, 1963) of 17 diffractometer settings each measured at $\pm 2\theta$. Intensities were measured on a Picker four-circle diffractometer with

Fe-filtered Co *K*α radiation ($\lambda = 1.7903$ Å). A unique data set was collected out to $2\theta = 130°$ by the θ–2θ scan technique with a scan range of 2° and a scan rate of 2°min^{-1}. Stationary background measurements were made for 10s on either side of each scan. 1311 non-zero reflections were corrected for Lorentz, polarization and background effects as well as for absorption (North, Phillips & Mathews, 1966).

The position of S was determined from a three-dimensional Patterson synthesis ($R = 0.59$). A heavy-atom-phased Fourier map revealed only four peaks significantly above noise level and these were identified as the O atoms of the sulphate ($R = 0.56$). One cycle of full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1961) of the parameters of the sulphate group reduced R to 0.50 and a Fourier calculation revealed the entire agmatine chain ($R = 0.44$). Refinement was continued and successive difference syntheses indicated the O atoms of two water molecules in the framework, and the H atoms close to their stereo-
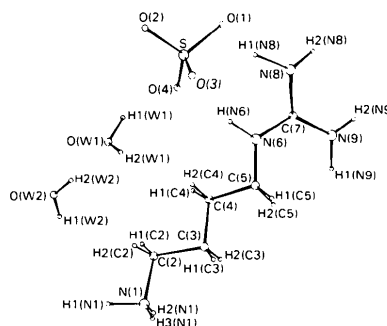
Fig. 1. Perspective view with atom-numbering scheme.