

(3,4-Dichlorophenoxy)acetic Acid

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Abstract. $C_8H_6Cl_2O_3$, m.p. 414–416 K, $M_r = 221.1$, triclinic, $P\bar{1}$, $a = 10.858$ (7), $b = 7.014$ (8), $c = 6.971$ (6) Å, $\alpha = 118.84$ (6), $\beta = 97.85$ (6), $\gamma = 97.99$ (7)°, $V = 447.7$ Å³, $Z = 2$, $D_x = 1.640$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.693$ mm⁻¹, $R = 0.058$ for 832 observed reflexions. The molecules form cyclic hydrogen-bonded dimers [O...O, 2.636 (4) Å] about a centre of symmetry in the cell. Unlike (2,4-dichlorophenoxy)acetic acid (2,4-D) and (2,5-dichlorophenoxy)acetic acid (2,5-D), the molecules are essentially planar, the dihedral angle between the planes of the benzene ring and the carboxylic acid group being 7.0 (5)° in comparison with 85.2 and 81.2° in 2,4-D and 2,5-D respectively.

Introduction. (3,4-Dichlorophenoxy)acetic acid (3,4-D) is a structural isomer of (2,4-dichlorophenoxy)acetic acid (2,4-D) and (2,5-dichlorophenoxy)acetic acid (2,5-D), both powerful auxin herbicides. Although it does not have the commercial importance of 2,4-D, 3,4-D has powerful herbicidal properties and has particular value as a wettable powder or paste of low water solubility for direct application to soils as a pre-emergence herbicide in regions of high rainfall (Crafts, 1957).

The crystal structures of both 2,4-D and 2,5-D are known (Smith, Kennard & White, 1976; Smith, Whitnall & Kennard, 1976) and have similar non-planar conformations. This is in contrast to the energetically preferred planar conformation of the parent phenoxyacetic acid and all other chlorophenoxy acids without 2,6-ring substitution (Smith & Kennard, 1979). The structure of this compound was determined to obtain more precise structural information on the substituted phenoxyacetic acid analogues.

Recrystallization of a sample of 3,4-D from a toluene–chloroform mixture provided crystals suitable

for X-ray examination. A single crystal (0.25 × 0.05 × 0.35 mm) gave 1044 reflexions (Syntex P2₁ four-circle diffractometer, graphite monochromator) of which 832 with $I > 1.5\sigma(I)$ were considered observed and used in structure solution and refinement. The automatic centrosymmetric \sum_2 sign-expansion procedure of SHELX 76 (Sheldrick, 1976) failed to solve the structure. However all non-H atoms were located using the tangent refinement method of SHELX. Full-matrix least-squares refinement with anisotropic temperature factors on all non-H atoms reduced $R[\sum |F_o| - |F_c|]/\sum F_o$ from an initial value of 0.32 to 0.058 and $R_w[\sum w|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2}$ to 0.054 [$w = 1.434/\sigma^2(F_o) + 4.66 \times 10^{-4}(F_o)^2$]. All H atoms except the carboxylic acid proton 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 Å². Neutral-element scattering factors were used for the non-H atoms (Doyle & Turner, 1968) while those for H were the Stewart, Davidson & Simpson (1965) values. No corrections were made for extinction or absorption effects [$\mu(\text{Mo } K\alpha) = 0.693$ mm⁻¹]. The maximum peak in the final difference Fourier map was equivalent to 0.118 e Å⁻³. Atomic positional parameters are listed in Table 1.† Interatomic distances and angles are shown in Fig. 1.

Discussion. The molecules of 3,4-D form planar centrosymmetric hydrogen-bonded cyclic dimers [O...O, 2.636 (4) Å] (Fig. 2). The dihedral angle between the planes of the benzene ring and the carboxylic acid group [7.0 (4)°] compares with 85.2° for 2,4-D (Smith, Kennard & White, 1976) and 81.2°

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35916 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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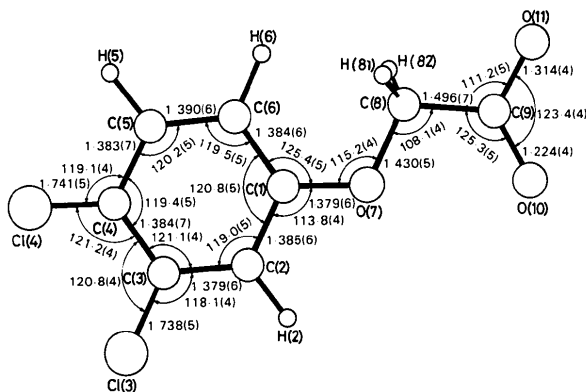


Fig. 1. Molecular conformation and atom-naming scheme with bond distances (Å) and angles ($^{\circ}$).

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 ²)
Cl(3)	5776 (2)	7801 (3)	1826 (3)	4.4 (1)
Cl(4)	5969 (2)	12874 (3)	3191 (3)	5.6 (1)
O(7)	8351 (4)	10394 (6)	9501 (6)	3.6 (3)
O(10)	9183 (4)	9024 (7)	12307 (6)	3.8 (3)
O(11)	10179 (4)	12525 (6)	15018 (6)	3.9 (3)
C(1)	7819 (6)	11138 (10)	8150 (9)	3.2 (4)
C(2)	7149 (6)	9429 (9)	6017 (10)	3.1 (4)
C(3)	6586 (5)	9973 (10)	4507 (9)	3.1 (4)
C(4)	6683 (6)	12183 (11)	5090 (10)	3.5 (4)
C(5)	7360 (6)	13876 (10)	7220 (10)	3.8 (4)
C(6)	7932 (6)	13359 (10)	8763 (9)	3.6 (4)
C(8)	9083 (6)	12117 (10)	11691 (9)	3.5 (4)
C(9)	9476 (6)	11033 (12)	12995 (10)	3.3 (4)
H(2)	7119	7838	5533	
H(5)	7424	15649	7875	
H(6)	8349	14715	10565	
H(81)	8494	13297	12591	
H(82)	9923	13078	11652	
H(11)	*			

* Not located.

for 2,5-D (Smith, Whitnall & Kennard, 1976). The conformation is similar to that found for phenoxyacetic acid (Kennard, Smith & White, 1981), the comparative torsion angles [C(2)–C(1)–O(7)–C(8), C(1)–O(7)–C(8)–C(9), O(7)–C(8)–C(9)–C(10)] about bonds in the oxoacetic acid side chains in the two acids (3,4-D and phenoxyacetic acid) being $+178.2$ (6), $+174.5$ (6), $+178.6$ (6) $^{\circ}$ and $+176.1$ (2), -175.1 (2), $+179.2$ (2) $^{\circ}$ respectively. Although the acid proton was not located, the carboxylic acid oxygens are identified as being carbonyl [O(10)] and hydroxyl [O(11)] on the basis of the angles C(8)–C(9)–O(10) [125.3 (5)] and C(8)–C(9)–O(11) [111.2 (5) $^{\circ}$]. These values are similar to those found for all known phenoxyalkanoic acids (Kennard *et al.*, 1981) and are

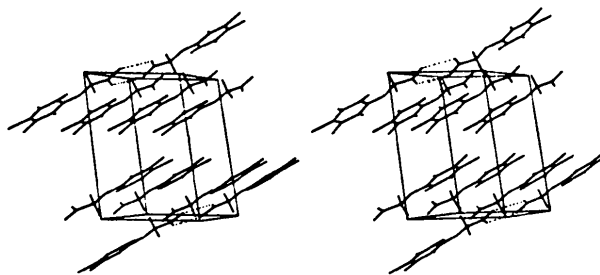


Fig. 2. Stereoview of the packing in the cell viewed down *b*; *a* is vertical and *c* to the right.

consistent with the mean values of 112 (2) and 123 (2) $^{\circ}$ obtained in an analysis of the geometries of the functional groups of carboxylic acids (Borthwick, 1980). Consequently the side-chain conformation is classified as synclinal–synclinal (carbonyl) which is common to all known phenoxyacetic and 2-phenoxypropionic acids with only one α -methyl substituent, and results in an intramolecular O(7)(ether)–O(10) distance of 2.671(4) Å.

Bond distances and angles for 3,4-D are considered normal for the phenoxy acids and within the phenoxy residue generally compare closely with those for 3,4-dichlorophenol (Bavoux, Perrin & Thozet, 1980). However, the distortion of the *exo*-C(1) angles, a feature among the phenoxy acids [125.4 (5), 113.8 (4) $^{\circ}$] [*cf.* 118.5 (6), 119.7 (6) $^{\circ}$ for 3,4-dichlorophenol], reflects the steric influence of the acetic acid side chain.

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